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Least Motion Paths in Unimolecular Decompositions[1]

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Abstract: Application of least motion analysis to unimolecular decomposition of simple large molecules suggests fragment center-of-gravity displacement to be a better choice of critical coordinate than extension of the breaking bond. For real molecules, outside the harmonic vibration region, however, explicit consideration should also be given to the latter. Quantitative estimations of the relative coordinate contributions, in terms of probabilities of decomposition, are presented for long-chain hydrocarbons under a variety of bonding conditions including surface attachment. The probabilities are obtained from a semiclassical (quantum statistical) model which it is shown connects directly to the least motion method. Fragmentation results are compared where possible with experiment, and the influences of neglected effects expected to be operative in real systems and various model simplifications are discussed.

The Principle of Least Motion (PLM), as it applies in the correlation of rates of related chemical reactions, has been the subject of a number of studies during the past decade.[2-5] Although severe applicability limitations have long been recognized, and rationalizations of correlational failures attempted, it is only recently that analytical means have been developed for separation of the constituents of the overall molecular distortions and their vibrational energy contributions, thereby facilitating detailed understanding of the correlational shortcomings. Derivation of closed-form motion equations of rather broad generality, consistent with harmonic springs modelling of reaction structure distortion, has allowed the importance of such factors as distortion mode, force constant and mass weighting, and the nature of end-point states to be identified.[6-8] These equations have likewise, and most important for present purposes, provided the means by which PLM may be applied to processes of a dynamical nature.

Specifically, and most noteworthy as a generalization, it was shown that to the extent the harmonic deformations around the reactant structures corresponding to appropriate normal modes of vibration persist in extension to the transition states, and that motions of the same kind are compared, satisfactory correlation of the unweighted motions with relative reaction rates could reasonably be expected. This generalization and others obtained rely strongly on identification of the individual atom motions, which differ to greater or lesser extent among the reactions to be correlated, and *how within the normal coordinates they couple* with the principal reaction coordinate motion which is common to all reactions compared.

In the present study, the analysis is directed to the important class of reactivities, unimolecular decompositions, considered as dynamical systems, with a particularly interesting general result emerging, relating to the existence of critical reaction coordinates of the Slater-theory type.[9] For dissociations characterized by the formation of fragment species with internal geometries not very different from the reactants, the least motion equations suggest critical separations of the centers-of-mass of the incipient fragments to be of at least comparable and perhaps of even greater importance than critical extension of the particular breaking bond in characterizing the probability (rate) of dissociation upon molecular excitation. This result supports and refines similar notions previously explored,[10] where equal dependence on the bond-breaking and centers-of-mass effects were hypothesized. The latter has been dubbed "the healing effect" for the obvious reason that the anticipated outcome of achieved critical extension of the breaking bond can be opposed and even overridden by unfavorable fragment center-of-mass motion, hence favoring reformation of the reactant or in more complicated situations isomeric forms thereof.

Some simple applications of the dual reaction coordinate model are presented where the relative effects of each may be conveniently gauged. Model truncation procedures are explored to assess the importance of structural details for the remaining (noncritical coordinate) elements of the reactant species. Other factors involved in unimolecular breakdown patterns, such as electronic and bond anharmonicity effects which can influence the degree of validity of the Principle of Least Motion as applied to reactivities, are briefly examined.

Reaction Coordinates from Least Motion Relationships

General Method and Derivations. Consider a molecule with N atoms undergoing molecular fragmentation by rupture of the bond between atoms t and $t + 1$, with atoms 1 through t in incipient fragment I and $t + 1$ through N in fragment II. From eq 1, 6, and 10 of ref 7, where the least motion relationships consistent with the harmonic springs ensemble model for such a reaction are obtainable, one may in straightforward fashion transform coordinates to the centers of gravity of the incipient fragments, *retaining the pure quadratic form (no linear displacement terms) of the original relationship.*

$$(D_\mu^2)_{R\gamma} = \sum_{i=1}^{N} \mu_i\{(p_i' - p_i)^2 + (q_i' - q_i)^2 + (s_i' - s_i)^2\} + M_{\rm I}\{(X_{\rm I'} - X_{\rm I})^2 + (Y_{\rm I'} - Y_{\rm I})^2 + (Z_{\rm I'} - Z_{\rm I})^2\} + M_{\rm II}\{(X_{\rm II'} - X_{\rm II})^2 + (Y_{\rm II'} - Y_{\rm II})^2 + (Z_{\rm II'} - Z_{\rm II})^2\} \quad (1)$$

Here, $p_i = x_i - X_K$, $q_i = y_i - Y_K$, and $s_i = z_i - Z_K$, where K is I for $t \geq i \geq 1$ and II for $N \geq i \geq t + 1$, and the upper case symbols (X, Y, Z) represent the center-of-gravity (CG) coordinate of the appropriate incipient fragment; e.g.,

$$X_K = \sum_{i}^{K} \mu_i x_i / M_K \quad (2)$$

where $M_K = \Sigma_i^K \mu_i$. The primes indicate the final state; the initial state coordinates are unprimed. Equation 1 implies all x, y, and z have been optimally transformed (translationally and rotationally to minimize D_μ^2) as dictated by eq 5 and 8 of ref 7. Linear terms it should be noted are absent since all are of the form constant $x\Sigma_{i=1}^{t} m_i p_i$, which are identically zero.[11]

Examination of eq 1 reveals the least-motion deformation $(D_\mu^2)_{R\gamma}$ depends upon the displacement terms for the individual atoms, relative to the center-of-gravity of the incipient fragments they occupy, plus terms for the displacement these centers of gravity experience during the reaction. We may therefore conveniently rewrite eq 1 as follows:

$$(D_\mu^2)_{R\gamma} = \sum_{i=1}^{N} \rho_i^{\,2} + M_{\rm I}\mathcal{R}_{\rm I}^2 + M_{\rm II}\mathcal{R}_{\rm II}^2 \quad (3)$$

noting that while the CG terms, $\mathcal{R}_K$, are simple distances in a set coordinate system, the ρ's are not, being referenced to moving coordinates (i.e., the fragments CG themselves).

In most unimolecular reactions, particularly where large molecules decompose to fragments which do not simultaneously rearrange and where the fissioning bond experiences the largest extension in the transition state, the second or fragment center-of-gravity displacement term would be expected to dominate. Therefore, to the extent the unimolecular reaction conforms to these conditions, the rate and hence the probability of the reaction should be directly dependent on the extent of separation of the centers of gravity of the entire fragments and not solely on the extension of the breaking bond (separations of atom t and $t + 1$) as formulated in Slater theory.

Two points raised in the above analysis require some amplification for intended applications here. The first is in the connection of the least motion measures $(D_\mu^2)_{R\gamma}$ with the relative probabilities of reaction. As usually employed, a smaller value of $(D_\mu^2)_{R\gamma}$ for geometrical distortion of a given initial to final state, compared to that for a second initial to final state change, is taken to imply a greater rate of reaction for the former process. Either the initial or final states, or both, may differ; the less difference in kind (stretches as distinct from bends, bends from torsions, etc.), the more confidence one should have in the least motion rate predictions forthcoming.[6,7] In the present context, it will be more convenient to initially consider the probability of a given distortion, specified as to extent as well as type, occurring in the course of vibrational excitation. Here then, greater probability for a distortion of specified magnitude attaches to the mode for which the greater distortion occurs *under equal excitation*. In turn, since a smaller $(D_\mu^2)_{R\gamma}$ indicates a greater rate in comparison of processes where equal critical mode distortion (i.e., extension of the breaking bond, increase in fragment CG distance) is assumed, greater distortion is expected in the more labile process for equal $(D_\mu^2)_{R\gamma}$. Hence, we would expect a greater probability for distortion of a given type and magnitude for that reaction mode which is characterized by the greatest rate and vice versa, expectations which certainly are in harmony with physical experience subject to the understanding that observed rates are dependent upon all populated vibrational modes of the reactant.

The second point recognizes the inclusion of a bond-break component of the Slater-theory type within the fragment center-of-gravity displacement terms. This fact and several others of imminent utility may be verified from examination of Figure 1, where two-dimensional representations of the CG relationships for a typical reaction are shown.

As it is generally appropriate to do, the centers of gravity of the whole-molecule initial and final states are located at the origin of this figure; the initial state CG vector is arbitrarily positioned along the x axis (I–II). That the final state vector (I′–II′) has a y component indicates that the reaction proceeds along a path where bending distortions within the fragments *and* between the fragments do not cancel; i.e., the fragment decomposition mode has a rotational component. It may be directly shown that for this case the CG displacement terms of eq 1 and 3 have the following relationship to the distances between them.

$$M_{\rm I}\mathcal{R}_{\rm I}^2 + M_{\rm II}\mathcal{R}_{\rm II}^2 = \mu_{\rm I,II}\{(d_t' - d_t)^2 + 2d_t d_t'(1 - \cos\alpha)\} \quad (4)$$

Respectively, d_t and d_t' are the distances between CG I and II and I′ and II′ for the fragments arising from scission of the bond between atoms t and $t + 1$, and $\mu_{\rm I,II}$ is the reduced mass of the fragments $M_{\rm I}M_{\rm II}/(M_{\rm I} + M_{\rm II})$. The angle α between the CG vectors arises from the contributions of the individual atom terms (the ρ's of eq 3) to the overall motion. In the event these atoms exhibit proportional rotation upon deformation to that of the CG vector, α will be zero. This, it will be recognized, is equivalent to a linear deformation of the whole molecule, that is, to the absence of a rotational component in the dissociation.

Also shown in Figure 1 are the positions of the atoms, t and $t + 1$, involved in the local break. Their positions (and weighting factors μ_t and μ_{t+1}) of course contribute to the positions of the CG's and hence, through rather complicated geometrical relationships for the general case considered, to the equality shown in eq 4 and, as well, in this situation, to the individual atom displacement terms of eq 1 and 3.

Particular Critical Coordinate-Probability Models. If we restrict ourselves at this point to consideration of dissociation cases not involving rotational components, i.e., to the most direct way angular momentum can be conserved, the analysis is much simplified. Here, the CG vectors and those describing the separations of the local-break atoms, t and $t + 1$, are colinear. Recollection of the assumption that the center-of-gravity terms should dominate in unimolecular fragmentation where rearrangement is precluded, as it is if the dissociation motion is restricted to be linear, leads from eq 1 and 3 to,

$$(D_\mu^2)_{R\gamma} \cong M_{\rm I}\mathcal{R}_{\rm I}^2 + M_{\rm II}\mathcal{R}_{\rm II}^2 = \mu_{\rm I,II}(d_t' - d_t)^2 \quad (5)$$

and, thence, under the previous arguments relating the probability, P_t, of related reactions to the extent of distortion under equal excitation, to

$$P_t = \text{direct function of } (D_\mu^2)_R = F\{\mu_{\rm I,II}(d_t' - d_t)^2\} \quad (6)$$

This relationship, the foundation of what shall be henceforward called model 1, implies that while the motions of atoms t and $t + 1$, (and hence the changing separation between them) contribute to the probability of the reaction, they do so exactly, except for differences in the weights, μ_i, as any other atoms through their influence on the fragment CG positions.

There are at least two reasons to suspect that this is an oversimplification, traceable at least in part to the small-vibration theory analogies upon which the least motion model is based. It has been shown that the least motion equations are proportional to those for the potential energy within vibration symmetry species, obtained with symmetry coordinate displacements,[7] but that the latter are linearly related to rectangular coordinate displacements *only as long as infinitesimal displacements are considered.*[12] In the dissociation process considered, clearly the displacements of atoms t and $t + 1$ cannot be so considered. Further, neither can this extension, leading to dissociation, be expected to conform as well to the harmonic approximation as the other nearest neighbor interactions. And, finally, although much more empirical in nature (in the sense of not deriving from the least-motion relationship), but at the foundation of Slater theory,[9] the separation of atoms t and $t + 1$, formally bound in the reactant, constitutes the operational observable for deciding whether dissociation has taken place.

Consequently, it seems reasonable to propose that the overall reaction probability $\mathcal{P}_t$ contain a term explicitly dependent upon the separation of atoms t and $t + 1$, that this term, π_i, be of the same form as the CG term previously derived, and, as well, that $\mathcal{P}_t$ have the functional form of a simple product, implying independence of the CG and explicit local break probabilities as befits the anharmonic correction function served by the latter. Allowing for different weighting of the critical coordinate contributions,

$$\mathcal{P}_t = P_t \cdot \pi_t{}^f \tag{7}$$

$$\pi_t = F\{\bar{\mu}_{t,t+1}(\delta_t{}' - \delta_t)^2\} \tag{8}$$

Here, $\delta_t{}'$ and δ_t are respectively the distances between atoms t and $t + 1$ in the initial and final states, f is the weight assigned the bond-breaking relative to the fragment CG effect, and $\mu_{t,t+1}$ is the reduced mass of the atoms t and $t + 1$. This model for the probability, model 2, it will be noted produces a relationship which is the square of that of eq 6 (model 1) for dissociation of a diatomic, as it should, and differs from the latter only in the weighting (μ) of the critical displacement when the geometries of the incipient fragments are maintained.

Relative Dynamical Reaction Probabilities

Finney and Hall have employed an empirical model for computation of the probability of unimolecular decomposition of one-dimensional harmonic oscillators under strong excitation[10] which is identical in critical coordinate specification to model 2. Their approach is semiclassical in that the classical equations of motion are assumed to describe the vibrations of the molecule, but that the quantum mechanical expectation values of the critical coordinates and the probabilities they are exceeded during vibration are taken to determine, proportionally, the probabilities of fragmentation. Their critical coordinates are the fragment CG and fissioning bond distances, and both probability functions are assumed to contribute equally to the overall probability of fragmentation.

In light of this correspondence, it seemed profitable to employ the Finney and Hall procedure, with appropriate modifications, to reinforce the previously undertaken extension of PLM into dynamical rate theory,[7] particularly into aspects of relative probabilities of reaction. The chemical system they examined, long-chain hydrocarbons fragmenting in the gas phase under excitation caused by electron impact ionization, has likewise been subjected to some simple modifications, such as surface attachment and internal bonding differences, both to aid in differentiation among the critical coordinate models and to extend their utility in chemical application. An outline of the procedure follows; following that the various model results and their implications are discussed.

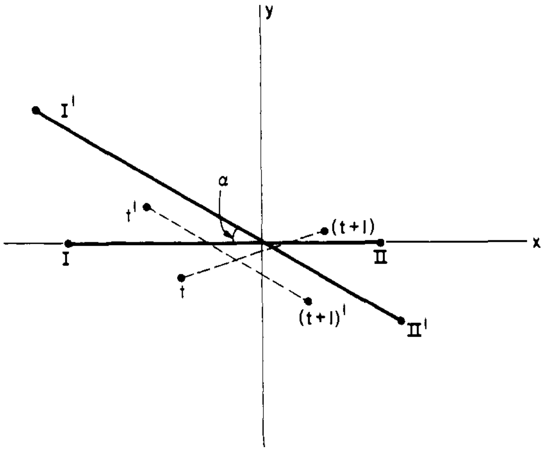

Figure 1. Representative fragment CG and local-bond displacement in a unimolecular decomposition process.

A linear array of N atoms, all of mass m and bound to nearest neighbors (distance a_e at equilibrium) by force constants, mk^2, obeys the classical equation of motion,

$$\mathrm{d}x_p/\mathrm{d}t = k^2(x_{p+1} + x_{p-1} - 2x_p) \qquad p = 1, N \tag{9}$$

where x is the displacement from the equilibrium position and the kinetic and potential energies of the system are,

$$T = \frac{1}{2} m \sum_{p=1}^{N} \dot{x}_p{}^2$$

$$V = \frac{1}{2} mk^2 \sum_{p=0}^{N} (x_{p+1} - x_p)^2 \tag{10}$$

The "imaginary" end atoms (p equal 0 and $N + 1$) are invoked to simplify the boundary conditions; if the molecule end is free, the displacement x_p of this end is taken equal to that of its neighbor; if bound to a surface x_p is zero. The general solution to eq 9 for the cases considered is,

$$x_p = \sum_{s=s_l}^{s_u} \alpha_s C(p,s,N) \exp(-2ik\omega(s,N)t) = \eta \sum_{s=s_l}^{s_u} C(p,s,N) Q_s \tag{11}$$

where the appropriate coefficients, exponents, normalization constants, and modes (s) are given in Table I. The Q_s are the normal modes of the system, and the α_s are the classical amplitudes.

As for the critical coordinates, it may be easily verified that $(R_t)_e = Na_e/2$, $(r_t)_e = a_e$, and

$$R_t - (R_t)_e = \frac{1}{N - t} \sum_{i=t+1}^{N} x_i - \frac{1}{t} \sum_{i=1}^{t} x_i \tag{12}$$

$$r_t - (r_t)_e = x_{t+1} - x_t \tag{13}$$

where R_t and r_t are respectively the fragment center-of-mass and local bond distances for molecules experiencing fission between atoms t and $t + 1$, and subscript e signifies the equilibrium condition.

The quantum mechanical wave functions for all the systems considered, which are solutions of the Schrödinger equation for coupled harmonic motions with the appropriate boundary conditions, are

$$\psi = KH_n(\xi_j) \exp\left(-\frac{1}{2} \sum_{s=s_l}^{s_u} \xi_s{}^2\right) \tag{14}$$

where H_n is the nth order Hermite polynomial, $\xi_s{}^2 = (2mk/\hbar)\omega(s,N)Q_s{}^2$, K is the normalization factor, and j signifies the one mode, s, assumed excited.

Table I. Coefficients for the Atom Displacements and for Determination of the Mean-Square Deviations of the Critical Coordinates[a]

One-Dimensional Chain System	s_ℓ, s_u η^2	$C(p,s,N)$ $\omega(s,N)$	$\frac{mkt^2(N-t)^2}{4\hbar} B^2_{s,t}$	$\frac{mk}{4\hbar} b^2_{s,t}$
Ends Free	$1, N-1$ $\frac{2}{N}$	$\cos\frac{(2p-1)s\pi}{2N}$ $\sin\frac{s\pi}{2N}$	$\frac{N\sin^2\left(\frac{ts\pi}{N}\right)}{4\sin^3\left(\frac{s\pi}{2N}\right)}$	$\frac{1}{N}\sin\frac{s\pi}{2N}\sin^2\left(\frac{ts\pi}{N}\right)$ [d]
One End Free [b]	$0, N-1$ $\frac{4}{2N+1}$	$\sin\frac{p(2s+1)\pi}{2N+1}$ $\sin\frac{(2s+1)\pi}{2(2N+1)}$	$\frac{2\left\{\begin{matrix} t\sin\frac{N(2s+1)\pi}{2(2N+1)} \sin\frac{N+1(2s+1)\pi}{2(2N+1)} \\ -N\sin\frac{t(2s+1)\pi}{2(2N+1)} \sin\frac{t+1(2s+1)\pi}{2(2N+1)}\end{matrix}\right\}^2}{(2N+1)\sin^3\frac{(2s+1)\pi}{2(2N+1)}}$	$\frac{2}{2N+1}\sin\frac{(2s+1)\pi}{2(2N+1)}\cos^2(2t+1)\frac{(2s+1)\pi}{2(2N+1)}$
Both Ends Bound [c]	$1, N$ $\frac{2}{N+1}$	$\sin\frac{ps\pi}{N+1}$ $\sin\frac{s\pi}{2(N+1)}$	$\frac{\left\{\begin{matrix} t\sin\frac{Ns\pi}{2(N+1)} \sin\frac{s\pi}{2} \\ -N\sin\frac{ts\pi}{2(N+1)} \sin\frac{(t+1)s\pi}{2(N+1)}\end{matrix}\right\}^2}{(N+1)\sin^3\frac{s\pi}{2(N+1)}}$	$\frac{1}{N+1}\sin\frac{s\pi}{2(N+1)}\cos^2(2t+1)\frac{s\pi}{2(N+1)}$

[a] See eqs. 11 and 17. [b] Bound to surface at atom 1 by force constant mk^2. [c] Bound to surfaces at atoms 1 and N by force constants mk^2. [d] Corrects the Finney and Hall result; the numerical coefficient of their last term in eq. 19 ref. 10, should be 16 rather than 4.

Upon recognition that the critical coordinates can be expanded in terms of the normal modes, e.g.,

$$\Delta R_t = R_t - (R_t)_e = \sum_{s=s_l}^{s_u} B_s(t)\xi_s \qquad (15)$$

and that, in general, the mean-square deviation of this coordinate is

$$\sigma^2(\Delta R_t) = \sigma^2(R_t) = \int\psi(R_t)^2\psi\,d\tau - \left(\int\psi R_t\psi\,d\tau\right)^2 \qquad (16)$$

$$= n_j B_{j,t}^2 + \frac{1}{2}\sum_{s=s_l}^{s_u} B_{s,t}^2 \qquad (17)$$

explicit evaluation of $a_c/\sigma(R_t)$ is direct and hence so is the probability of the critical coordinate exceeding a_c, viz.,

$$P(R_t) = \frac{1}{\sqrt{2\pi}}\int_{a_c/\sigma(R_t)}^{\infty}\exp(-y^2/2)\,dy$$

$$\sim \frac{1}{\sqrt{2\pi}}\frac{\sigma}{a_c}\exp\left(-\frac{a_c^2}{2\sigma^2}\right) \qquad (18)$$

$$\ln P \sim -\ln(a_c/\sigma) - a_c^2/2\sigma^2 \sim -a_c^2/2\sigma^2 \qquad (19)$$

for $\sigma \ll a_c$, as is generally the case. Exactly the same equations are derivable for the bond break term, with r_t (and $b_{s,t}$) replacing R_t (and $B_{s,t}$). The $B_{s,t}$ and $b_{s,t}$ terms upon which the probabilities depend are to be found in Table I.

At this point, the functional relationship (F) required in eq 6 and 8 to bring the *static* (D_μ^2) probability dependences into correspondence with those of the *dynamic* model may be specified and the influence of the reduced-mass factors assessed. If $(d_t' - d_t)^2$ and $(\delta_t' - \delta_t)^2$ of eq 6 and 8 are interpreted to be the average values of the squares of the fragment CG and bond-breaking coordinates for a dynamic (vibrating) system experiencing a given excitation, then $\sigma^2(d,t) = \langle(d_t' - d_t)^2\rangle$ and $\sigma^2(\delta,t) = \langle(\delta_t' - \delta_t)^2\rangle$. (The average values of these coordinates are zero, as befits a harmonic or other even function.) If, then, a Gaussian probability distribution is assumed, as in eq 18, consistent with large coordinate extension for reaction, the fraction of oscillators with critical coordinates extended by an amount equal to or greater than a_c is $E(\sqrt{a_c^2/\sigma^2})$, where E is the error function. In the static model, a_c may be interpreted as the extension of the critical coordinate from its equilibrium value to that in the transition state. Assuming this extension, i.e., the positions of the respective transition states, to be independent of which bond is being broken, and recognizing that $d_t' - d_t$ and $\delta_t' - \delta_t$ are identical respectively to ΔR_t and Δr_t, the static and dynamic models are seen to coincide, and the function F becomes that of eq 18.

The appearance of reduced-mass factors $\mu_{\text{I,II}}$ and $\mu_{t,t+1}$ in eq 6 and 8, respectively, are consistent with the static interpretation of the least motion models. Equation 5, from which eq 6 directly derives, has the form of the potential energy for a pseudodiatomic (i.e., the two fragments of masses M_{I} and M_{II} located at their respective fragment CG's) with force constant implicit. Equation 8 may be assumed to arise by similar considerations of the pseudodiatomic composed of the atoms t and $t+1$. Upon viewing the long-chain fragmentations in terms of these two particle models, henceforth called $\bar{1}$ and $\bar{2}$, potentially useful approximations to the relative critical coordinate probability effects of models 1 and 2 may be derived as follows.

In close analogy to the development for the individual atom chain,

$$T = \tfrac{1}{2}(m_1\dot{x}_1^2 + m_2\dot{x}_2^2)$$
$$V = \tfrac{1}{2}[(f_1 + f_{12})x_1^2 - 2f_{12}x_1x_2 + (f_2 + f_{12})x_2^2] \qquad (20)$$

where it is now more convenient to write the composite force constants with mass dependences included,[13] and where f_1 and f_2 are respectively these constants for attachment to the appropriate surfaces, assumed to be infinitely massive. The quantum mechanical wave functions, ψ, here, solutions of the Schrödinger equation,

$$-\frac{\hbar^2}{2}\left(\frac{1}{m_1}\nabla_1^2 + \frac{1}{m_2}\nabla_2^2\right)\psi + V\psi = E\psi \qquad (21)$$

are exactly of the same form as eq 14, but where $\xi_s^2 = \bar{\omega}_s Q_s^2$ and,

$$\bar{\omega}_s = \hbar^{-1}\sqrt{\lambda_s} \qquad (22)$$

$$\lambda_{1,2} = \frac{1}{2m_1m_2}\{m_1(f_2 + f_{12}) + m_2(f_1 + f_{12})$$
$$\pm([m_1(f_2 + f_{12}) - m_2(f_1 + f_{12})]^2 + 4m_1m_2f_{12}^2)^{1/2}\} \qquad (23)$$

The mean-square displacements, equivalent to σ^2, may then be written as,

$$\bar{\sigma}_t^2 = \langle(x_1 - x_2)^2\rangle = (n_1 + \tfrac{1}{2})\beta_{1,t} + (n_2 + \tfrac{1}{2})\beta_{2,t} \qquad (24)$$

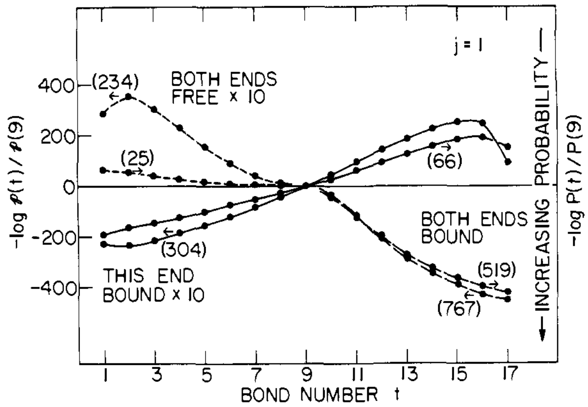

Figure 2. Fragment CG and total probability profiles for decomposition of long hydrocarbon chains ($N = 18$) ionized and vibrationally excited (fifth overtone, $n = 6$). Excitation is in the low mode, $j = 1$.

where

$$\beta_{s,t} = \left(\frac{d_t}{m_{3-s}{}^{1/2}} + \frac{(-1)^s}{m_s{}^{1/2}}\right)^2 \Big/ (1 + d_t{}^2) \qquad (25)$$

$$d_t = \frac{f_{12}/(m_1 m_2)^{1/2}}{[(f_1 + f_{12})/m_1] - \lambda_1} = -\frac{f_{12}/(m_1 m_2)^{1/2}}{[(f_2 + f_{12})/m_2] - \lambda_2} \qquad (26)$$

Results and Discussion

The system chosen by Finney and Hall, that is the 18 carbon atom chain (normal octadecane, $C_{18}H_{38}$), subjected to 50-eV electron impact ionization which causes subsequent fragmentation, is entirely satisfactory for the present illustrative purposes and is therefore chosen for initial examination. Their physicochemical constants were also adopted for the numerical calculations.[14]

In Figures 2-4, relative log P and log $\mathcal{P}$ values, for models 1 and 2, respectively (from the full expression, eq 18, and assuming equal weight for the local break term, $f = 1$, in the latter) are plotted vs. t for several choices of mode excitation (j, see eq 14), for all three systems (ends bound or free). The results are typical of those obtained with intermediate modes and for minimum excitations greater than the fundamental ($n_j > 1$).

In all cases, with the exception of the lowest normal mode, the unbound molecule is predicted to have a greater probability (more negative value in the figures) for rupture near its ends. On the other hand, molecules which are bound to a surface should prefer to break in the middle, or if one end is free near this end. These conclusions follow from consideration of either model 1 or 2. Upon excitation of a very high normal mode, however, even molecules bound at both ends will begin to show a preference for end breaks (see $j = 16$ case) over the middle, which in turn, at least in the composite effect model 2, are predicted to remain more probable than at intermediate positions (atoms 5-8 and 10-13). Excitation of the lowest normal mode leads, it would appear, to just the opposite conclusions. It should be noted, however, that variations in CG and total probability with changing t are very small for the systems with one or both ends free and that the overall probabilities of fragmentation when both ends are bound are likewise very small.[15] It is also useful to note that while this mode represents a symmetric all-bonds-in-concert stretch for the free molecule, it does not for the bound molecules. The difference in predicted behavior for the free molecule from that reported in ref 10 is due to the correction noted in Table I.

Of equal interest are the relative contributions of the CG and local break effects, both of which are available, the latter by difference from these figures. It is apparent that for the lower normal modes the differential CG effects are dominant; i.e., the composite model 2 results parallel for the most part those of the CG model 1. Minor exceptions are noted for the free molecule cases for $j = 1$ and 2. In both cases, extrema in the local-break probabilities are reflected in the composite results near the ends, whereas the CG effects are monotonic. For the higher normal modes, the local-break effects often show greater differences. For $j = 16$, for example, the latter effect is sufficiently structured, compared to that from the CG displacement, to give the bimodal probability function for the bound molecules and to change the sign of the curvature for the free species. Nevertheless, these are properly recognized as fine structure effects, not mitigating the gross end vs. middle bond break conclusions previously drawn.

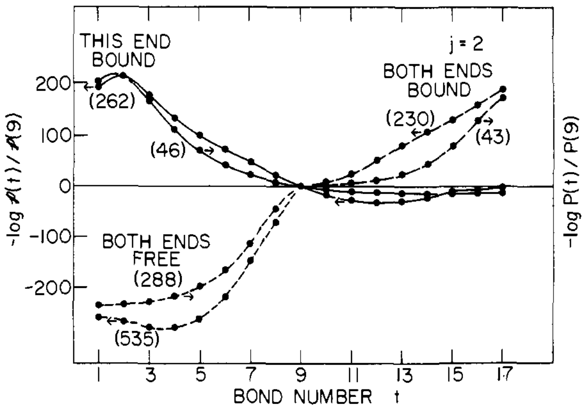

Figure 3. See caption of Figure 2. Excitation is in the next-lowest mode, $j = 2$.

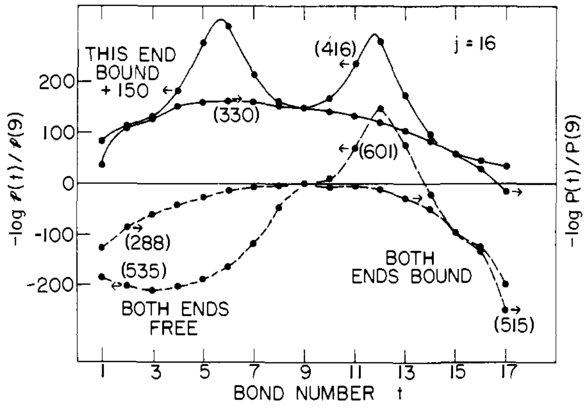

Figure 4. See caption of Figure 2. Excitation is in the high mode, $j = 16$.

Direct experimental evidence to test these predictions is unfortunately scanty, particularly for the bound molecule cases. Free gas-phase molecules are known to break preferentially near their ends (t equals 3 or 4)[16] in agreement with the results obtained here and despite electronic effects which appear to work in the opposite direction (i.e., greater charge removal upon ionization and hence greater bond weakening near the center of the molecule). Such nonvibrational effects have been considered in ref 10. For molecules bound to surfaces, comparable data do not now appear to be available but may soon be from mass spectrometric field desorbtion studies.[17] Surface catalytic cracking of hydrocarbons is also a process to which the models examined should pertain. For example, for SiO_2-Al_2O_3-ZrO_2 catalysts, attachment to the surface is presumably followed by hydride removal, producing an attached carbonium ion which subsequently decomposes to an olefin and a smaller carbonium ion.[18] Cracking of n-hexadecane at 500 °C, for example, is purported to yield C_4 fragments in greatest abundance (followed by C_3 and C_5 fragments),[19] in apparent agreement with the one-bound-end model discussed.[20] The agreement may, however, be fortuitous, in that the model predicts the end furthest from the surface to be the one most probable to break (strongly for the $j = 2$ mode, less so for the $j = 16$ mode), whereas analysis of cracking data usually invokes what is known as the β rule, electronic in origin, not vibrational, which puts the position of break close (β positional) to the binding site. The implication follows that initial binding is in fact not at the end of the molecule at all but rather at the internal sites, hydride removal by the surface being favored from CH_2 rather than CH_3 groups.

One other body of data may be presented for comparison, which, despite complications perhaps as severe as those encountered above, can improve perspectives of the fragmentation process. Gamma radiolysis of liquid long-chain alkanes produces a fragmentation pattern which is strongly peaked at the middle product radical mass range.[21] This observation is in agreement with the model results for molecules with both ends bound. While the containment of an activated chain species by solvent is not obviously similar to the specified site (both ends) binding model considered, assumption that the most important solvent cage effects are exerted at the ends should not be any more serious than representation of the molecule as one dimensional in the first place. Restriction of one-dimensional vibrations should be much more important in the normal than parallel direction to these vibrations. Interestingly, for real three-dimensional molecules, linear fragmentation (along the vector connecting the fragment CG's in the initial state) should lead directly only to radical products upon escape of the cage; fragmentation occurring with a rotational component would be expected to produce as well isomers of the original hydrocarbon or alkenes upon disproportionation within the cage. Evidence to distinguish these modes is unfortunately unavailable.

By means of perturbation theory, the model calculations described may be made to closer approximate other potentially interesting experimental systems, particularly involving the surface-bound substrates. Brief mention is made of the results obtained for molecule chains where regular (periodic) differences in force constants pertain. A particular case of interest is where the period equals the number of atoms in the chain with both ends bound to the surface, which corresponds to weaker (or stronger) end attachment than internally. The method involves use of quantum mechanical perturbation theory to obtain the new ψ (eq 14) which is familiar[22] and of classical perturbation theory to obtain the new normal modes Q_s (eq 15)[23] which is not. The results obtained indicate that weakening (or strengthening) of the surface-attachment bonds (force constants, k') should increase (or decrease) the $B_{s,t}{}^2$ and $b_{s,t}{}^2$ coefficients through factors $(1 + \delta T_s)$ where $\delta = 1 - (k'/k)^2$ and T_s is principally a function of the composite motions of the atoms in the unperturbed chain with respect to, and weighted inversely by their distances from, the points of attachment. Hence, for the lower modes, the greatest magnification occurs for those modes where the atoms move in concerted fashion, with symmetric motion with respect to the walls having the greatest effect. These are intuitively reasonable results, as are those which predict the higher mode perturbations, T_{N+1-j}, to be approximate reflections of the corresponding lower mode effects, T_j. The effects of periodic weakening or strengthening of the internal bonds, also available by the method outlined, are of interest for such real systems as polymer and polypeptide fragmentation. While somewhat more complicated than the end effects just discussed, the perturbations appear to be exercised on the σ^2 coefficients, particularly for the free-molecule chains, in essentially an additive fashion, making the probabilities of scission of weaker bonds proportionally more likely.

Exactly similar methods may be applied to evaluate the effects of bond anharmonicities. Such considerations are, however, beyond the scope of this paper, since the principal concern here is to explore the utility of critical coordinate models for unimolecular reactivities within the harmonic approximation. Nevertheless, it is useful to note that such effects would be reflected in substantial mixing of the normal modes and by overall bond loosening, complicating features in the probability approach taken, and, as well, that cubic (odd) anharmonicity terms which would contribute to the free-molecule probabilities are absent for molecules bound at both ends.

Returning to the original simple harmonic hydrocarbon chain systems, the results for the united-atom fragment models ($\overline{1}$ and $\overline{2}$) are usefully compared with those having the full atom structure explicit. For the free molecule, it may be easily shown $\overline{\sigma}^2(R_t)$ and $\overline{\sigma}^2(r_t)$ are both expressible as $(n_2 + {}^1/_2)\hbar/k\mu$, where μ is the appropriate reduced mass and n_2 is the degree of excitation of the symmetric-stretch mode. For the fragment CG probability, where $\mu_{\mathrm{I,II}} = t(N - t)/N$, $-\log \overline{P}$ varies roughly as $a_c{}^2/2\overline{\sigma}^2$, or proportional to $t(N - t)/N$, in agreement with the full-structure results which predict a higher probability for end- than central-bond scission. Interestingly, the value of $-\log \overline{P}$ (9) for the central bond, with $n_2 = 6$, for comparison with the parenthesized values of Figures 2–4, is 216, and the variation with t is concave downward, resembling the $j = 16$ mode behavior.

For the local break effect, if the masses of atoms t and $t + 1$ pertain, the probability function would be *invariant with t*. If, alternatively, the total masses of the fragments are assigned to these sites, the behavior becomes identical with that just observed for the CG coordinate. The latter assignment, it might be noted, has been suggested elsewhere in connection with calculation of isotope effects from a Slater-type critical coordinate model.[24] Neither assumption is capable, however, of reproducing the full structure local break results; generally the latter are characterized by minima part way along but not at the center of the chain.

Application of models $\overline{1}$ and $\overline{2}$ to the surface-bound species presents even more provocative results. If the force constants of eq 20 are set proportional to the reduced masses of the particles involved in each bond which appears reasonable, f_1, f_{12}, and f_2 are respectively $M_{\mathrm{I}}k^2$, $\mu_{\mathrm{I.II}}k^2$, and $M_{\mathrm{II}}k^2$ $(mtk^2$, $mt(N - t)k^2/N$, and $m(N - t)k^2)$ in the case of both ends bound and for the CG critical coordinate. The $\overline{\sigma}^2(R_t)$ dependence here is $(n_2 + {}^1\!/_2)\hbar/\sqrt{2}k\mu$, identical with that for the free molecule except for the factor $2^{-1/2}$ and hence clearly at variance with the model 1 result. Albeit more complicated, largely because both $\beta_{1,t}$ and $\beta_{2,t}$ are nonzero and vary differently with t, the one-end-bound results under the same force constant assumption are also found to be in disagreement with those where full structure is considered. In both cases, scission near the bound end would appear to be preferred.

What is likely most seriously wrong here is the assumption that the force constants for attachment to the surfaces are constant except for the mass effect, neglecting the fact that the equilibrium (initial state) distances between the walls and fragment CG's vary strongly with t. (Recall, from eq 12 and relations leading thereto, that the equilibrium distances between fragment CG's are t invariant, always being $Na_e/2$.) If one assumes something like a Badger's rule dependence upon distance to attempt correction of this deficiency relative to the full structure model, where, of course, attachment is always at the end atom and consequently not dependent on t, considerably different results are obtained. Figure 5 displays the $-\log \overline{P}$ (and $-\log \overline{\overline{P}}$) results obtained when the force constants are all assumed to vary inversely as the cube of the distance (and, as before, directly with the reduced mass). This distance dependence, it will be recognized, is less severe than Badger's rule.[25] The overall probability functions now appear in satisfactory agreement with those obtained with the full structure models; see in particular the $j = 2$ case, Figure 3, and recognize that this is the highest (and for the free chain, the only vibrational) mode available for excitation in the pseudodiatomic model.

The free chain profile is, of course, unaffected by the force-constant-upon-distance dependence. When both ends are attached, the force constant binding the fragment CG to the walls, always stronger than that between the CG's, increases rapidly as the pseudoatom position approaches the wall. Since the force constant for binding the *other* fragment to the *other* wall decreases, but only very much more slowly, the effect of this movement (t going from $N/2$ downward, for example) is to essentially immobilize fragment 1, while only enhancing the motion of fragment 2 slightly. Hence, the probability for scission decreases with t decreasing from the center and since when both ends are bound the system is symmetric, with increasing t, as well. Only for $t = 1$ (and $N - 1$) is there an exception, mainly due to the mass effect which decreases the rate of force constant strengthening. In contrast, in the local-break model the force constants for surface attachment are always very small except for t equal 1 or 2. Consequently, the results for bonds near the chain center resemble those for the free molecule (no t dependence) and only vary (become less probable) right near the surfaces because of the immobilization effect mentioned above. The trend here persists to $t = 1$ because there is no mass effect.

When only one end is bound, proceeding from the chain center toward the surface produces similar effects to those delineated above. Varying t toward the free end has the other effect, in that the force constant for the fragment nearest the surface decreases, but here there is no overriding surface effect from the other (f_2 is zero). Consequently, scission at this end is predicted to become increasingly more probable.

It seems reasonable to conclude, on the basis of the above comparisons, that while the free chain probabilities are largely reflections of mass effects, particularly for the CG critical coordinate, there are internal motion effects in the fragments which more than overcome the influences of mass when the chain vibrations are altered by end attachment to surfaces. (One might well have inferred such differences in internal motions of the fragments based upon the behavior of the center-of-mass of the reactant chain; when attached to one or more surfaces of infinite mass this point can move substantially without violating traditional constraints.) Further, the results of these motions appear to be representable, at least grossly, by modification of the vibration undergone by the conglomerate mass located at the fragment CG, depending on the distance the latter is from the surface, attachment to which is responsible for the internal motion difference. Comparably satisfactory adjustment of the local break profile cannot however be attained by similar force constant upon distance specification. Again, this is not particularly surprising since all structural information about the incipient fragments of which the t and $t + 1$ sites are terminal members is neglected, in contrast to the fragment CG models (1 and $\bar{1}$) where for both structural averages pertain.

Conclusions

Least motion analysis of paths for unimolecular decomposition of simply structured large molecules suggests that incipient fragment center-of-gravity separation is a reasonable choice of critical reaction coordinate, although contributions of the more conventional local break coordinate may also be necessary. From the point of view of small vibration theory as employed in the least motion procedure, the CG coordinate incorporates much of the behavior of the constituent atoms in the dissociating fragments, ignoring only relatively smaller effects (differential changes of atom positions with respect to the fragment CG's) whose signs are known. In contrast, consideration of only the dissociating bond ignores potentially important effects within the fragments, which may (because of linear terms in $D_\mu{}^2$ transformed to these coordinates) operate to decrease or increase the least motion estimate of reaction progress. Nevertheless, because the final (transition) state generally involves relatively large distortions of the breaking bond, explicit inclusion of this coordinate is probably necessary.

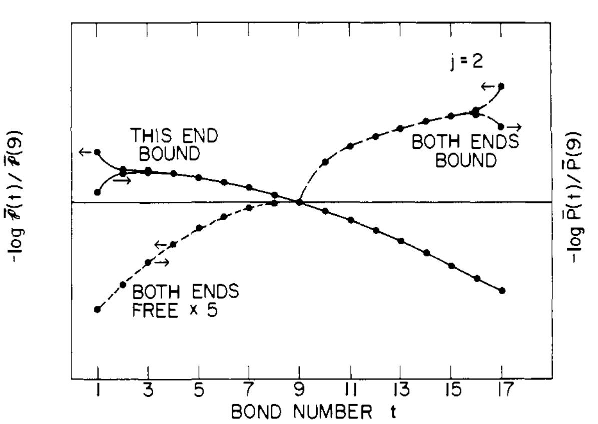

Figure 5. Fragment CG and total probability profiles for the $N = 18$ hydrocarbon chains in the pseudodiatomic, variable force constant model approximation.

More quantitative estimates of the relative effects of CG and local atom motions, obtained as semiclassical reaction probability contributions, indicate that at least in one-dimensional motion, the CG effects are more structure dependent and, hence, important, even though the local break is necessary for reaction and capable of modifying to some degree the probability profile. Acceptance of the fragment CG motion as a critical coordinate leads directly to an acceptable mechanism for bond healing; even upon large extension of the local bond, reaction may not take place if the fragment CG's are not themselves also largely extended. The implication of such opposed effects to two or more dimensional systems and under various bonding constraints, where isomerization as well as healing can occur, are usefully considered.

Specification of the fragment CG motion as critical, it should be recognized, implies the motions of the individual atoms are unimportant to reaction probability except as they determine the motions of these CG's. This has been shown to be an acceptable approximation within the least motion framework. The further approximation that it is only the masses of these atoms and the positions they occupy in the initial reactant state which are important has also been examined, with generally negative results. It appears that while specification of the individual atom motions determining the CG positions may not be explicitly required, adjustments of binding to what are essentially frozen fragments may be necessary. Only the roughest details of the probability profiles, however, may be reproduced by such adjustments. No reasonable remedy of the gross inadequacies of the local break model, observed under this approximation, are possible.

Attachment to a surface at one or more points is predicted to grossly affect vibrationally induced molecular motion along critical coordinates and, hence, not surprisingly, the modes of decomposition followed. These effects, as distinct from those of purely electronic origin accompanying surface attachment, may well be predominant in catalysis even though the mechanism of attachment is found to depend entirely on the latter. Unfortunately, however, the clarity of such distinctions as these, and for that matter intramolecular comparisons, may be obscured by anharmonicity effects, which although vibrational are outside the purview of the least motion method employed.

References and Notes

(1) Research carried out at Brookhaven National Laboratory under contract with the U.S. Energy Research and Development Administration.
(2) J. Hine, *J. Org. Chem.*, **31**, 1236 (1966); *J. Am. Chem. Soc.*, **88**, 5525 (1966).
(3) S. I. Miller, *Adv. Phys. Org. Chem.*, **6**, 185 (1968).
(4) O. S. Tee, *J. Am. Chem. Soc.*, **91**, 7144 (1969).
(5) O. S. Tee and K. Yates, *J. Am. Chem. Soc.*, **94**, 3074 (1972).
(6) S. Ehrenson, "Chemical and Biochemical Reactivity", Proceedings of the International Jerusalem Symposium, 6th, 1974, pp 113–130.
(7) S. Ehrenson, *J. Am. Chem. Soc.*, **96**, 3778 (1974).
(8) S. Ehrenson, *J. Am. Chem. Soc.*, **96**, 3784 (1974).
(9) N. B. Slater, "The Theory of Unimolecular Reactions", Cornell University Press, Ithaca, N.Y., 1959; *Proc. R. Soc.* (*London*), *Ser. A*, **194**, 112 (1948).
(10) R. D. Finney and G. G. Hall, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 489 (1970).
(11) One may rather easily show that the same overall (whole molecule) center-of-gravity conditions are required for transformation to this new fragment coordinate system from arbitrary positioning of the initial and final species and that appropriate rotation by the angle γ will accomplish rotational optimization where both states share a plane of symmetry (have at least C_s symmetry), where

$$\tan\gamma = \frac{\sum_{i=1}^{N} \mu_i(\bar{q}_i\bar{p}_i' \mp \bar{p}_i\bar{q}_i') + \sum_{K=1}^{2} M_K(\bar{Y}_K\bar{X}_{K'} \mp \bar{X}_K\bar{Y}_{K'})}{\sum_{i=1}^{N} \mu_i(\bar{q}_i\bar{q}_i' \pm \bar{p}_i\bar{p}_i') + \sum_{K=1}^{2} M_K(\bar{Y}_K\bar{Y}_{K'} \pm \bar{X}_K\bar{X}_{K'})}$$

The barred coordinates are those which are obtained following the whole-molecule CG (translational) transformations.
(12) See. e.g., G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, N.Y., 1945, pp 142–147.
(13) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross. "Molecular Vibrations", McGraw-Hill, New York, N.Y.. 1955, pp 28–31.
(14) For $C_{18}H_{38}$, $m = 1.993 \times 10^{-23}$ g, a_c, the critical coordinate extension, one equilibrium bond length (a_e. which is 1.55×10^{-8} cm), and the force constant $mk^2 = 5 \times 10^5$ erg cm^{-2}. The minimum degree of excitation accompanying ionization, n, is 6, obtained as for a pseudodiatomic from $\Delta E = nh\nu$, where ΔE is the difference in vertical and photoionization potentials, extrapolated from known values for smaller hydrocarbons, and ν is the frequency of the C–C alkane bond; $\hbar = 1.054 \times 10^{-27}$ erg s. Note, of course, that *n*-alkanes while "linear" chains are not one-dimensional vibrators but have bending modes. They are the closest real molecule analogues to the models, however. Likewise, it should be apparent that *temporal* correlation of favorable local break with unfavorable CG motions, and vice versa, cannot be made with these models which employ expectation values of critical coordinate functions.
(15) The figures given in parentheses are the $-\log P$ (or $-\log \mathcal{P}$) values for the central bond. While the absolute values of these numbers have little meaning because other factors on the rate such as collision frequencies have not been considered, their relative values should, and the large numbers obtained for the molecule with both ends bound suggests a very improbable process.
(16) F. H. Field and J. L. Franklin, "Electron Impact Phenomena", Academic Press, New York, N.Y., 1957.
(17) See, for example, H.-D. Beckey, "Field Ionization Mass Spectroscopy", Pergamon Press, New York, N.Y., 1971, pp 306–308.
(18) J. E. Germain, "Catalytic Conversion of Hydrocarbons", Academic Press, New York, N.Y., 1969, Chapter 4.
(19) A. Van Hook and P. H. Emmett, *J. Am. Chem. Soc.*, **85**, 697 (1963).
(20) Excitation to a lower n than 6 is probably called for here, the process being much gentler than electron impact ionization. Examination of the relative probabilities for lower n reveals almost identical patterns. E.g., for $n = 2$, with the exception of some minor curvatures at the extremes, the probability functions appear identical but require scaling by ~0.8. Hence the previous conclusions require no modification.
(21) R. H. Schuler and R. W. Fessenden, Proceedings of the Third International Congress on Radiation Research, Cortina, Italy, 1966: see also, R. A. Holroyd, "Fundamental Processes in Radiation Chemistry", Interscience, New York, N.Y., 1968. p 461.
(22) See, e.g.. L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics". McGraw-Hill, New York, N.Y., 1935, Chapter 6, Section 23.
(23) J. W. Strutt (Baron Rayleigh), "The Theory of Sound", Vol. 1, Dover Publications, New York, N.Y., 1945. Chapter 4, Section 90.
(24) M. Wolfsberg, *J. Chem. Phys.*, **33**, 21 (1960).
(25) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, 1960, p 231.

Mechanism of Ozonolysis. Ab Initio Study of the Primary Ozonide and Its Cleavage to the Criegee Intermediate

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Abstract: Part of the ozonolysis reaction has been investigated by means of an ab initio SCF MO theory. Several possible primary ozonides have been tested and the 1,2,3-trioxolane, with an O-envelope conformation, is retained as being slightly more stable than the C–C half-chair and planar forms. Two state correlation diagrams show that the planar cleavage is thermally forbidden and that the envelope 1,2,3-trioxolane can collapse, by a symmetry allowed 1,3 dipolar cycloreversion, to the Criegee zwitterion. The activation energy of this process has been estimated by a CI calculation and is consistent with the instability of the primary ozonide.

I. Introduction

The mechanism of the ozonolysis of olefins, both in liquid and gaseous phase, has been a subject of wide interest. Many proposals have been put forward, but all of them involve a more or less modified Criegee[2] mechanism, at least as a competing pathway. In its original form, it is simply suggested that the ozone molecule adds to the olefin to form a 1,2,3-trioxolane ring (**1**), which cleaves to give a zwitterionic methylene peroxide and an aldehyde. These two products react further to give the final ozonide (**2**). But some facts are not explained by this simple scheme; in particular, it is known that the cis/trans ratio of the final cross ozonide depends on olefin geometry.[3] This led Story, Murray, and Youssefyeh to propose a so-called "aldehyde interchange" mechanism,[4] in which an aldehyde can be incorporated in the 1,2,3-trioxolane ring. In addition, they suggest a more direct pathway for sterically hindered cis olefins, via the σ complex (**3**), to account for the high cis/trans ozonide ratio[4] obtained with bulky cis olefins, as well as the high yields of ozonides.[3a,b] On the other hand, Bauld, Bailey, and co-workers proposed a revised version of the Criegee