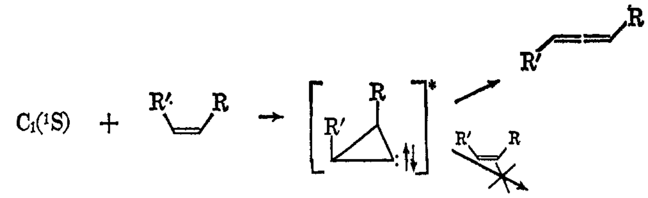
The energy of activation for rearrangement must be greater than the energy of activation for addition to another molecule of olefin (Figure 1). At room temperature in solution rearrangement of singlet cyclopropylidenes to allenes takes place readily,[15–18] in competition with olefin addition.

The ^{1}S atom addition to an olefin should have a formal resemblance to the ^{1}D addition, the major difference being the 33-kcal/mole extra energy brought to the transition state by the higher energy atom. If this hot singlet cyclopropylidene were an intermediate of lifetime sufficient to permit trapping by olefins, the yields of allenes would vary with changing the substituents R and R′ since these substituents would be expected to influence the rate of ring opening to the allene. This is not the case, the yields of allenes being 40–47% with the variation in substituents reported here. Thus it follows the hot singlet cyclopropylidene is not a trappable intermediate. For ^{1}S + olefin the cyclopropylidene configuration may only represent a transition state.



Since the activation energy for ring opening of a normal singlet cyclopropylidene (from ^{1}D) is small, the species in the reactions of C$_1$(^{1}S) may bypass this configuration and go directly to the allene; the hot species may not be able to lose its surplus energy fast enough to lead to a thermally equilibrated cyclopropylidene intermediate.

The relative reactivities of olefins in competition for ^{1}S atoms is not highly informative since the spread of reactivities is small. Perhaps it is most significant that butadiene is less reactive than monoolefins, ruling out transition states with radical character.

An interesting and disturbing feature of these matrix systems must relate to their physical nature. The striking differences in reactivity of CH$_3$ groups for ^{1}S insertions in neopentane and isobutane was noted earlier in this study. Perhaps for related reasons the double bond of 1-butene is more reactive than those in propene, 1-pentene, and 1,5-heptadiene (terminal bond). No electronic rationalization of this effect is apparent.

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research and the Army Research Office (Durham).

A Simple Theory for Predicting the Effects of Substituent Changes on Transition-State Geometry[1,2]

Edward R. Thornton

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania. *Received December 5, 1966*

Abstract: A simple technique for analyzing the effects of substituent changes on transition-state geometry is outlined. The basic idea is to consider the effects of substituents as linear perturbations of the vibrational potentials for the normal coordinate motions both parallel to and perpendicular to the reaction coordinate motion. Effects parallel to the reaction coordinate then correspond closely to predictions based on "Hammond's postulate," while effects perpendicular to the reaction coordinate introduce a previously neglected effect which is expected to be smaller than the parallel effect in many, but not all, cases. Examples of application of the theory to SN2, E2, SN1, and other reaction mechanisms are presented. The theory is discussed in terms of the forces on nuclei predicted by the Hellmann–Feynman theorem. Using precise potential energy curves for diatomic molecules calculated by computer from spectroscopic data, it is concluded that the approximation that the perturbation is linear, if a relatively small substituent change is made, is probably a very good one. The result is: (1) any substituent change which makes an increase (decrease) in the normal coordinate X of a molecule or transition state more difficult will lead to a perturbed equilibrium geometry in which X is decreased (increased) if the force constant for X motion is positive, but in which X is increased (decreased) if the force constant for X motion is negative; (2) the effect of a substituent change on a normal coordinate motion can be predicted from the effect of the substituent on the reacting bond(s) nearest to the substituent and involved in that motion; (3) when two reacting bonds are equidistant from the substituent, the effect of the substituent should be nearly equal on both if both are of the same strength in the unperturbed transition state, but should be greater on the stronger than on the weaker (and greater on a σ than on a π bond); (4) an electron-supplying (withdrawing) substituent should make a bond more difficult to extend (compress) if attached to the basic, *i.e.*, more electronegative atom, end of the bond, but more difficult to compress (extend) if attached to the acidic, *i.e.*, less electronegative atom, end of the bond; (5) the substituent effect on geometry is the sum of individual effects on each normal coordinate.

Since substituent effects upon a stable molecule's structure, energy, and other properties are reasonably well understood in a qualitative way, it is fascinating to try to apply this qualitative understanding to predict the effects of the substituents on the structure, energy, and other properties of transition states, or

---

(1) Supported in part by the Atomic Energy Commission (Contract No. AT(30-1)-3041) and by the National Science Foundation (Grants No. GP-2937 and GP-6047).

(2) *Cf.* (a) L. J. Steffa and E. R. Thornton, to be published; (b) G. J. Frisone and E. R. Thornton, to be published.

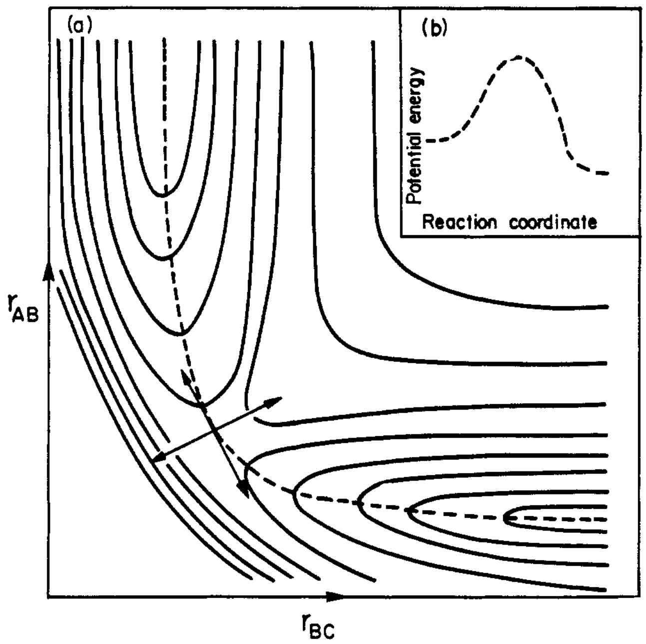


Figure 1. (a) Contour surface for the reaction A + BC → AB + C. Contours of constant (electronic) potential energy for nuclear displacement plotted as a function of the bond distances r_{AB} and r_{BC}. The reaction coordinate is the dashed line. Parallel and perpendicular motions are shown as double-headed arrows. The reaction is assumed to proceed without any bending of the ABC angle from 180°, so that the potential energy depends only on r_{AB} and r_{BC}. (b) Plot of potential energy *vs.* distance along the reaction coordinate.

activated complexes, for various reactions. The relative success of transition-state theory[3] in describing and making predictions about rates and mechanisms of thermal reactions, together with the considerable (though approximate) theoretical justification of the method, make it reasonable to discuss reaction mechanisms in terms of a transition state of definite geometry corresponding to the point of highest electronic energy[4] along the most favorable path by which reacting molecules may be converted into products. Other, necessarily higher energy, reaction paths exist which do not pass through the transition-state geometry.

The motion corresponding to the reaction coordinate which has negative restoring force at the transition state is shown as a dashed line in Figure 1 for the simple case of a linear approach of A to BC, A displacing C.

Since a transition state is defined as being at a potential energy extremum (saddle point) and, therefore, its internal nuclear motions consist of vibrations analogous to the normal vibrations of stable molecules in the sense that, at the geometry of the extremum, no forces act on the nuclei, it is not unreasonable to suppose that structural predictions based on principles established for stable molecules would carry over in considerable detail to transition states. The "Hammond postulate"[5] and various extensions[6] have been used to make predictions about transition-state geometry from reactant, intermediate, and/or product geometries and enthalpies of reaction. A noteworthy, early example of the application of principles similar to those of the Hammond postulate is the explanation of the Brønsted catalysis law[7] in terms of the crossing of potential energy curves for the bonds being made and broken in a proton-transfer reaction, *e.g.*

$$\mathrm{B} + \mathrm{HA} \text{—}[\mathrm{B}\text{- - -}\mathrm{H}\text{- - -}\mathrm{A}]^{\ddagger} \longrightarrow \mathrm{BH} + \mathrm{A}$$

Although these generalizations seem fundamentally reliable, certain experimental results seem to conflict[8] with predictions, and a "rule" has been suggested[8] which seemed to correlate all known data. In analyzing the results of our[2a] and other studies of E2 (elimination, bimolecular) reactions, certain ambiguities and inconsistencies were discovered. A major ambiguity is that the statement of this rule[8] in terms of "reacting bonds" and "reacting orbitals" implicitly assumed that there was only one reacting bond in a single reacting orbital, whereas E2 transition states clearly involve more than one. It might be possible to modify the rule to eliminate the ambiguity. However, the present author believes there are inconsistencies in the (admittedly *a posteriori*) theoretical model, the major one being the assumption that because supplying electrons to, say, the X group of a X–Y bond is expected to make that bond longer at the transition state (of a reaction in which that bond is being made or broken), the increased X–Y bond length implies a decreased electron supply at Y. It now seems almost certain that supply of electrons to X would, while increasing the X–Y bond length, nevertheless *increase* the electron supply at Y;[9] the predictions of the rule would then be reversed in certain cases.

Although approximate models tend to justify it, an assumption equivalent to the idea that "if a bond is

---

[3] *Cf.* S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941; H. Eyring, D. Henderson, B. J. Stover, and E. M. Eyring, "Statistical Mechanics and Dynamics," John Wiley and Sons, Inc., New York, N. Y., 1964; H. Eyring and E. M. Eyring, "Modern Chemical Kinetics," Reinhold Publishing Corp., New York, N. Y., 1963; K. J. Laidler and J. C. Polanyi, *Progr. Reaction Kinetics*, 3, 1 (1965); J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963; M. M. Kreevoy in "Investigation of Rates and Mechanisms of Reactions," Part II, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter XXIII; also several other chapters in Parts I and II; "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962; D. Rapp, "On Experimental Tests of the Validity of the Transition State Theory of Chemical Reaction Rates," Report 6-90-62-126, Lockheed Missile and Space Company, Sunnyvale, Calif., 1962; H. S. Johnston, *Advan. Chem., Phys.*, 3, 131 (1960); "Gas Phase Reaction Rate Theory," The Ronald Press Co., New York, N. Y., 1966; V. N. Kondrat'ev, "Chemical Kinetics of Gas Reactions," Pergamon Press and Addison-Wesley Publishing Co., Inc., Reading, Mass., 1964; E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964.

[4] The electronic energy as a function of nuclear geometry is, of course, in the (Born–Oppenheimer) approximation that electron motion is always very fast relative to nuclear motion, used as the potential energy for nuclear motions.

[5] G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955): "If two states, as, for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of the molecular structures." A less well-known, but earlier, statement of a similar principle is given by J. E. Leffler, *Science*, 117, 340 (1953).

[6] K. B. Wiberg, *Chem. Rev.*, **55**, 733, 737 (1955); A. Streitwieser, Jr., *ibid.*, **56**, 571 (1956).

[7] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter X; R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, Chapter VIII; J. Horiuti and M. Polanyi, *Acta Physicochim. URSS*, 2, 505 (1935); R. P. Bell, *Proc. Roy. Soc.* (London), **A154**, 414 (1936).

[8] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 817 (1962).

[9] This conclusion can be approximately justified by considering that the primary effect will be electron supply to X and therefore to Y. The primary effect will be partly offset by the secondary effect of increased X–Y bond length, but only partly offset because in the Born–Oppenheimer approximation electron motions determine the motions (and, therefore, the average positions) of the nuclei, not the other way around.

made harder to break, it will become more broken at the transition state" is usually required for such predictions. This type of assumption is very hard to justify in its stated form because of the property of a transition state that its energy is the *minimal* energy *maximum*, *i.e.*, the maximum barrier required by the most favorable reaction path. Expressing the properties of functions which have simultaneous minima in one or more dimensions and maxima in another is difficult to do in any way which leads to generalizations.

The problems which arose in application of the above generalizations made it seem likely that a new approach was required. The basic innovation of the "rule" was consideration of transition-state structural effects directly, rather than by comparison with reactants, products, or intermediates, all of which differ in energy by relatively large amounts from the transition state.[10] Direct prediction of the effect of substituents on transition-state structure, if possible, was clearly desirable. It further became obvious that previous generalizations had largely considered such effects in terms of geometric changes "along the reaction coordinate," *i.e.*, changes in fraction of product-like character of the transition state, and had all but ignored effects upon normal modes of *vibration* of the transition state, *i.e.*, shifts of the transition-state geometry perpendicular to the reaction coordinate. These "parallel" and "perpendicular" directions are shown as arrows in Figure 1, corresponding to the tangent to the reaction coordinate at the transition-state point and the perpendicular to the tangent. In the simple case illustrated in Figure 1, where there are only two geometric variables —the two bond lengths—it can be seen that the parallel motion stretches one bond while compressing the other, and the perpendicular motion either stretches or compresses both bonds simultaneously.

A simple perturbation method has emerged which (at least in principle) takes account of both parallel and perpendicular shifts in transition-state geometry. It is outlined, illustrated, criticized, and approximately justified in the following sections.

Simple Perturbation Method. In analyzing the effect of a substituent on a transition state, we are interested in determining the effect on each bond in turn. This would be quite straightforward for a stable molecule (assuming one had adequate empirical and theoretical data to predict how a substituent (say, electron supplying) should change the force constant or bond strength for each type of bond). For a transition state there is the complication that motion of the nuclei along the reaction coordinate is not a truly vibrational motion (it has a negative restoring force), though motion corresponding to all the other normal vibrations of the transition state is truly vibrational (with positive restoring force). Substituent effects upon motions with positive and negative restoring forces turn out to have opposite geometric effects; therefore, one must consider which nuclei actually move in the reaction coordinate motion.

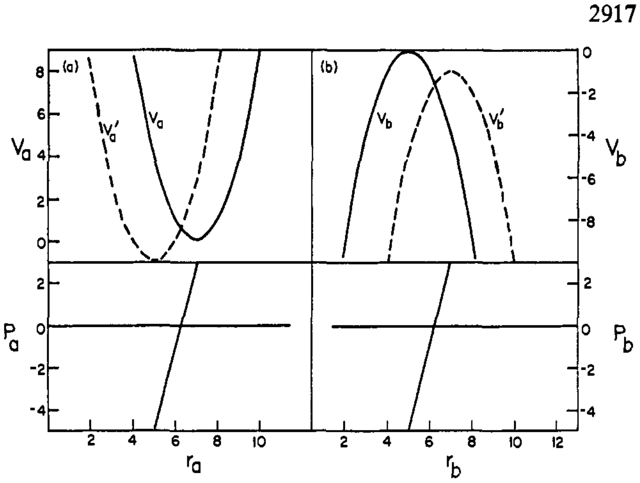


Figure 2. Plots of parabolic potentials, V, together with the perturbations, P, which, when added to V, give the new parabolic potentials, V'. Note that the slope of P_a is exactly equal to the slope of P_b. (a) Effect expected for perpendicular motion; (b) effect for parallel motion.

All nuclei of the transition state may in principle move during the reaction coordinate motion (though some may be prohibited from moving by symmetry), but the major displacements will undoubtedly be of those nuclei which participate in bonds that are being made or broken during the course of reaction. Such *reacting bonds*[8] can be singled out for study. It can be assumed that groups attached through nonreacting bonds to the nuclei involved in the reacting bonds will approximately follow along with those nuclei as the reacting bonds undergo reaction–coordinate motion. Furthermore, if the reaction coordinate motion involves largely changes in length of reacting bonds (as would be the case in many reactions), bending motions may reasonably be left out of consideration. The case where only one reacting bond is present (relatively unusual) is simplest. In this case the only important motion corresponding to the reaction coordinate is the stretching (for a dissociation reaction) or compression (for an association reaction) of the reacting bond. A plot of energy *vs.* bond length will then look like the curve in Figure 1b, but the abscissa will not be the curved reaction coordinate shown for the displacement reaction of Figure 1a; the abscissa will simply be the length of the reacting bond.

The vibrational energy of a molecule is a nearly quadratic function of the displacement of the nuclei from their equilibrium positions. The effect of a substituent upon one of the bonds of a molecule is to make small changes in energy, equilibrium bond length, and force constant. Since such effects are relatively small, it can be expected that they will be approximately described by the addition of a linear function of distance to the reference, "unperturbed" curve.[12] The result for a model with a parabolic potential energy function and an exactly linear perturbation is shown in Figure 2a. The shift in the energy of the extremum is caused mainly by the vertical position of the linear perturbation, but the extremum also shifts to longer or

---

(10) The danger of "crossover" effects (or even "double-cross" effects) in the potential energy curves for differently substituted systems is considerable in some cases.[11]

(11) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1962, p 93; R. D. Brown, *Quart. Rev.* (London), **6**, 72 (1952).

(12) This aproach was originally suggested by a discussion of secondary isotope effects in terms of such perturbations, given by E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963). A similar technique has also been used for discussion of the changes in geometry and energy of ordinary molecules upon addition or removal of an electron to form ions and upon electronic excitation: J. P. Malrieu, *Theoret. Chim. Acta*, **4**, 434 (1966).

shorter bond length. The same perturbation in fact causes a greater shift of bond length the less the curvature of the unperturbed curve, as will be shown below. The effect of substituents on bond geometry can, therefore, be predicted (approximately, of course) as in Figure 2a by empirically or theoretically estimating the slope (sign and magnitude) of the perturbation. Although it is assumed that the perturbation is linear, the *direction* of the effect is dependent mainly on the slope (positive or negative) of the perturbation at the point of the unperturbed extremum.

In the case of Figure 2a, if we assume that the perturbation slope was caused by adding an electron-supplying substituent to the molecule, it can be interpreted as follows: the electron-supplying substituent makes bond extension more difficult and bond compression easier. Such an effect probably explains the effects of substituents on the O–H stretching vibrations of substituted phenols;[13] electron-supplying substituents in the phenyl ring increase the vibration frequency.

In the case of a transition state, the potential energy as a function of distance along the reaction coordinate (Figure 1b) can be approximated as an inverted parabola in the region of the potential energy maximum, as shown in Figure 2b. There is no theoretical reason why the effects of substituents in perturbing the potential energy along the reaction coordinate should be different from substituent effects on true molecular vibrations. The same linear perturbation shown in Figure 2a produces the dashed curve of Figure 2b, and it can be assumed with considerable confidence that the resulting change in geometry would be observed for a substituent change which made motion (from left to right) along the reaction coordinate *more difficult*.

Empirical data, which will aid in making predictions about ionic reactions where charge accumulation or dispersal occurs, are available; prediction is more difficult for radical or molecular reactions. Hopefully, further data on stable molecules, such as effects of substituents on vibrational frequencies, will give predictions of the direction of the perturbation for most kinds of bonds.

The basic ideas described can readily be applied to reactions having more than one reacting bond. Several reacting bonds can be considered simultaneously by considering the normal vibrations of the transition state and estimating the effects of substituents on the normal vibrations,[14] *e.g.*, the parallel and perpendicular motions in Figure 1a. Each normal vibration can be considered to have a potential energy curve as a function of normal coordinate displacement similar to Figure 2a, except the reaction coordinate motion, which will be similar to Figure 2b.

In many cases only the reacting bonds closest to the substituent will be important in determining the perturbation, provided one can estimate their relative displacements in the normal coordinate motions. It is essential to consider at least two reacting bonds simultaneously if they are equidistant from the substituent, *e.g.*, if substitution were made at B in the reaction A + BC → AB + C, where AB and BC were reacting bonds and are equidistant (both terminate at atom B) from the substituent.

The net effect of a substituent on transition-state geometry can be obtained by estimating the position of the perturbed extremum along each normal coordinate as in Figure 2 and then adding the effects for all normal coordinates to find the total. Again it should be noted that, to a very good approximation, only those normal coordinates involving reacting bonds and/or nuclei near the substituent will add appreciably to the total.[15] The ideas just described are best explained by concrete examples, but before discussing examples, some of the qualitative ideas suggested should be examined in more detail.

The constructions in Figure 2 can be expressed algebraically. If the unperturbed extremum is placed at the origin, the assumption that the unperturbed curve is parabolic and that the perturbation is linear gives

$$V = {}^1/_2kX^2$$

$$P = mX + b \qquad (1)$$

$$V' = {}^1/_2kX^2 + mX + b \qquad (2)$$

where V is the unperturbed energy (solid line), k is the force constant (>0 for Figure 2a, <0 for Figure 2b), X is the deviation of the normal coordinate from its equilibrium value (the equilibrium geometry is usually defined as $X = 0$ for all normal coordinates of a molecule), P is the (linear) perturbation, m the slope and b the intercept of P, and V' is the perturbed energy (dashed line). By setting the derivative of V' with respect to X equal to zero, the extremum of the perturbed curve (which is also a parabola) can be seen to be[12] at

$$X_{\mathrm{ex}} = -m/k \qquad (3)$$

For example, positive m gives a shorter bond for positive k, a longer bond for negative k, as shown in Figure 2. The shift in energy of the extremum is, substituting eq 3 into eq 2

$$V'_{\mathrm{ex}} = b - m^2/2k$$

It can be seen from eq 3 that at constant m the shift of bond length is greater for smaller absolute values of k. Also the curvature or force constant is given by the second derivative of V with respect to X and can be seen to be unchanged (k) on going from the unperturbed to the perturbed curve. It can be seen that if the perturbation were given by a smooth curve rather than a straight line, the curvature of the perturbed curve V' would be different from k, but that the *direction* of the shift X_{ex} would depend only on the slope (positive or negative) of the perturbation at $X = 0$, the position of the unperturbed extremum, even though the perturbation were nonlinear.

Since it is known that real molecules have potential curves that are fairly well represented by parabolas, and since molecular anharmonicities are always in the same direction, the perturbation P is likely to be a very nearly linear function. It then seems interesting to see

---

(13) L. L. Ingraham, J. Corse, G. F. Bailey, and F. Stitt, *J. Am. Chem. Soc.*, **74**, 2297 (1952).

(14) This, of course, assumes that the forces are simply harmonic, *i.e.*, linear in displacement, and so is an approximation. Also, it will be noted that this is a classical, not quantum mechanical, idea. However, the quantum mechanical solution of the problem of describing nuclear vibrations nevertheless utilizes normal coordinates.

(15) A striking example of such a "cutoff" procedure's having negligible effects upon kinetic isotope effect calculations is given by M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225, 325 (1964).

what results if P is linear but the potential function V is somewhat anharmonic, as the next better approximation to substituent effects. In this case an anharmonic term proportional to X^3 should be added, giving

$$V = {}^1/_2kX^2 + gX^3$$
$$P = mX + b$$
$$V' = {}^1/_2kX^2 + gX^3 + mX + b$$

where g is the anharmonicity constant. Now setting the derivative of V' with respect to X equal to zero, the extremum of the perturbed curve can be seen to be at

$$X_{\text{ex}} = [-k + (k^2 - 12mg)^{1/2}]/6g$$

for positive k and at

$$X_{\text{ex}} = [-k - (k^2 - 12mg)^{1/2}]/6g$$

for negative k. The force constant for both curves V and V' is given by $k + 6gX$ and is thus a function of X. For the unperturbed extremum ($X = 0$), the force constant is k. For the perturbed extremum ($X = X_{\text{ex}}$), the force constant is $(k^2 - 12mg)^{1/2}$ for positive k and $-(k^2 - 12\ mg)^{1/2}$ for negative k. This model gives a shorter bond for positive m and k, just as the previous harmonic model did. The anharmonic model is more realistic, at least for bond stretching vibrations, in predicting a smaller absolute value of force constant for greater X (since g is negative for bond stretching). It is expected that longer bonds (positive X_{ex}) will both be weaker and have weaker force constants.

A very interesting point is that, apparently, anharmonicity of V should be more important in determining the change of force constant upon substitution than nonlinearity of the perturbation, for the following reason. It can be expected that the nonlinearity of P will be in the direction that it will drop off more slowly or increase less slowly as X increases (for bond stretching), reaching an asymptotic value at the separated atoms, *i.e.*, complete bond rupture. But this direction is such that it would tend to increase the force constant for positive X_{ex} (negative m, for positive k) and decrease the force constant for negative X_{ex} (positive m, for positive k). This direction is opposite to what is physically expected, that longer bonds are in general weaker and have weaker force constants. It must, therefore, be concluded that the anharmonicity represented by g will usually override the possible effect of nonlinearity of P!

The other point that should be justified is that the total effect of the substituent can be obtained by summation of the effects predicted for individual (harmonic) normal coordinates. By definition the individual P effects contribute additively to the energy.

$$V' = \sum_i({}^1/_2k_iX_i^2 + m_iX_i + b_i)$$

The extremum of a function of more than one variable is given by setting the partial derivative of the function with respect to each variable equal to zero

$$m_i + k_iX_i = 0 \text{ (for all } i)$$

Thus the perturbed extremum is at the position

$$(X_i)_{\text{ex}} = -m_i/k_i$$

of each normal coordinate (neglecting anharmonicity), *i.e.*, at the point of the potential energy hyperspace with "coordinates" (V'_{ex}, $(X_1)_{\text{ex}}$, $(X_2)_{\text{ex}}$, $\ldots(X_i)_{\text{ex}}$ $\ldots$ $(X_{3N-6})_{\text{ex}}$), since a nonlinear molecule has $3N - 6$ normal vibrations. The position in hyperspace can be reached by vector addition of the displacements $(X_i)_{\text{ex}}$. For example, with two normal coordinates (as in Figure 1) the perturbed extremum is reached by moving along X_1 to $(X_1)_{\text{ex}}$ and then perpendicular to X_1 (*i.e.*, in the direction of X_2) to a distance of $(X_2)_{\text{ex}}$, or equivalently along X_2 first, then perpendicular to X_2. The result of such a movement to the new extremum in hyperspace can be described in three-dimensional space, of course, since the $(X_i)_{\text{ex}}$ are known functions of the $3N$ coordinates of the N nuclei. The effects of each normal coordinate shift upon each of the three coordinates of each nucleus can be simply added together to produce the total shift of that coordinate of that nucleus.

For the harmonic approximation, the normal coordinates associated with the perturbed extremum are exactly the same as the X_i (for the unperturbed extremum). This must be so, because all masses and force constants are unchanged. It can easily be shown that if new normal coordinates are defined as

$$X'_i = X_i - (X_i)_{\text{ex}}$$

then

$$V' - V'_{\text{ex}} = \sum_i {}^1/_2k_i(X'_i)^2$$

and, therefore, the X'_i are indeed normal coordinates (an alternative definition of normal coordinates being that the potential energy is proportional to the squares of the coordinates, with no cross-terms proportional to X_iX_j).

Rule for Predicting Geometric Changes. The predictions of this theory can be stated concisely. Any substituent change which makes an increase (decrease) in the normal coordinate X of a molecule or transition state more difficult will lead to a perturbed equilibrium geometry in which X is decreased (increased) if the force constant for X motion is positive, but in which X is increased (decreased) if the force constant for X motion is negative.

It remains to decide whether a given substituent change will make the increase or the decrease of a given normal coordinate X more difficult. Qualitatively, it would appear reliable to consider the individual bonds which are being stretched or compressed in motion X; further, the major effect should be upon those reacting bonds which are closest to the substituent. Nonreacting bonds which are close to the substituent could, of course, be considered but will usually be ignored in practice, and the reacting bonds will be singled out for study, as discussed in the previous section.

The valence-bond concept pictures bonds with varying amounts of covalent and ionic character. It is found, at least for diatomic molecules, that bonds between unlike atoms show greater bond energy than might be expected for "homonuclear-type" covalent bonds[16] (*e.g.*, as calculated for bond A–B from the geometric mean of the A–A and B–B bond energies). This "excess" bond energy can be attributed to ionic character, tending to stabilize bonds between unlike atoms, and has been used as a definition of electro-

---

(16) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, Chapter 3.

negativity.[16] A reasonable extrapolation suggests that any substituent change which makes a given bond "more homonuclear", *i.e.*, lessens ionic character, will tend to make that bond more difficult to compress (and weaker). For example, in the molecule

$$\underset{\delta^+}{\mathrm{A}}\text{---}\underset{\delta^-}{\mathrm{B}}$$

where the atom of group B which is bonded to group A is assumed to be more electronegative than the atom of group A to which the former is bonded, it is predicted that an electron-supplying substituent would (a) if in group B tend to make both B and A more negative but have a larger effect on B than A, thus increasing ionic character and making the A–B bond more difficult to extend (and, of course, easier to compress), or (b) if in group A tend to make both B and A more negative but have a larger effect on A than B, thus decreasing ionic character and making the A–B bond more difficult to compress (and, of course, easier to extend). There is one point where electronegativities of the free atoms may not give proper results: if the substituent change also changes the charge type. The electronegativity of the atom "in the molecule" is what is needed. For example, the following substituent change

$$\mathrm{C{-}Cl} \longrightarrow \mathrm{C{-}N^+(CH_3)_3}$$

where the C–Cl and C–N bonds are reacting bonds and where Cl and N both have electronegativity 3.0 as elements, is a case where one would have to be very careful in making predictions. The charge distribution changes from the Cl substituent's being negative relative to carbon to the $N^+(CH_3)_3$ substituent's being positive relative to carbon, even though the positive nitrogen should be more electronegative than 3.0. In such a case, it is probably best to use the acid–base properties ($N(CH_3)_3$ being a stronger base than Cl^- in usual types of solvents), as discussed in the next paragraph. Obviously the solvent effect will be quite strong here, for polar solvation will affect little the basicity of neutral bases and decrease the basicity of negatively charged bases. The substituent effect in the gas phase could be different—even opposite—from the effect at the other extreme, say extrapolated to infinite dielectric constant. The effects for real solvents would be between the extremes, but difficult to predict theoretically. The experimental criterion of basicity can be tentatively used, but its reliability can and should be tested experimentally. Such problems as this arise only when the substituent change is unusually drastic, almost never unless one of the atoms of a reacting bond is changed.

Acid–base concepts lead to the same predictions. In the above example, B would be pictured as the basic group since it is more electronegative than A; A would be pictured as the acidic group. Supply of electrons to B should make it more basic and make the A–B bond more difficult to extend, while supply of electrons to A should make it less acidic and make the A–B bond more difficult to compress. Basicity toward a proton seems to be a good criterion[8] and has the advantage of simplicity: *e.g.*, absence of steric effects. Other workers have concluded[17] that leaving group ability is a more appropriate criterion, on the basis that leaving group ability, measured for the reaction in question, takes account of steric effects. However, the theory described in the present paper takes account of steric effects directly by consideration of their effects on normal vibrations; it is thus more appropriate to have a measure of electrical effects which includes as little steric component as possible.

It is important to keep separate the two aspects of this theory. The first, the idea of estimating the perturbation and adding it to the unperturbed curve, is a rigorously correct approach because the perturbation (though the correct perturbation may not be linear) is *by definition* the difference between the unperturbed and the correct perturbed curve. The second aspect, the ideas that the perturbation may be considered nearly linear and that the slope of the perturbation may be estimated from ordinary bonding concepts, may have exceptions. The crucial question in the latter case is probably whether the bonding concepts which are reasonably reliable for stable molecules can also be applied to transition states. We believe and assume that they can, because as long as one is considering *differences* between substituents, there seems to be no theoretical reason that transition-state effects should differ from stable molecule effects. The only source of difficulty would seem to be if the usually long, weak reacting bonds in a transition-state structure were sufficiently different from the usually shorter, stronger bonds in stable molecules that certain predictions were made incorrectly. All indications are that there is a continuous change in bonding with bond distance,[18] however.

One other point should be mentioned, that the predictions made are for changes in transition-state structure, while most experimental information (rates, solvent effects, Brønsted coefficients, kinetic isotope effects) refers to the difference between reactant(s) and transition state. The correct approach would be to make predictions for all normal coordinates of both reactant(s) and transition state. However, it can be expected that *substituent* effects on nonreacting bonds will be small and also nearly the same for reactant and transition state. Evidence that this is so comes from studies of substituent and solvent effects on secondary deuterium isotope effects;[19] such effects are quite small. These effects could nevertheless be estimated by the present theory provided the perturbations for reactant and transition state could be predicted accurately. It is the reacting bonds which differ greatly from the bonds of the reactant(s),[20] being much weaker in the transition state (for bonds being broken) or much stronger in the transition state (for bonds being made). Also, since the transition-state reacting bonds will be weak in most cases, substituent effects on geometry are expected to be much larger than for ordinary, strong bonds because the curvature k of the potential

---

(17) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *J. Am. Chem. Soc.*, **87**, 1553 (1965).

(18) For example, it has been shown that Badger's rule for predicting force constants from bond lengths is reliable not only for ground states of molecules, but also for excited states and even van der Waals interactions: R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935); *Phys. Rev.*, **48**, 284 (1935); D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **35**, 458 (1961); H. S. Johnston, *J. Am. Chem. Soc.*, **86**, 1643 (1964).

(19) W. E. Buddenbaum, Ph.D. Thesis, University of Indiana, 1964; V. J. Shiner, Jr., and G. S. Kriz, Jr., *J. Am. Chem. Soc.*, **86**, 2643 (1964); G. J. Frisone and E. R. Thornton, *ibid.*, **86**, 1900 (1964).

(20) Unless the transition state is exceedingly reactant-like, in which case *no* substituent effect difference between reactant(s) and transition state is predicted.

energy function will be less for normal coordinates involving weak bonds (*cf.* eq 3). To the extent that substituent effects on reactant bonds are very small,[21] which should be true except when the substituent change actually changes one of the atoms of the bond being considered (*e.g.*, comparison of C–Br with C–Cl), the effects observed experimentally will be predicted by consideration of substituent effects on the transition state only.

Examples. The above method of predicting substituent effects is in agreement with Hammond's postulate[5] in all cases where the substituent effect is expected to be largely along the reaction coordinate—which are in fact the only cases for which the Hammond postulate was developed—but also, upon inclusion of perpendicular effects, is in agreement with all reasonably unambiguous experimental evidence on substituent effects.

One important example is SN2 nucleophilic displacement. A displacement reaction is illustrated in Figure 1, and it can be seen that the normal coordinates of the transition state are approximately

$$\longleftarrow A \qquad \longleftarrow B \quad C \longrightarrow$$

perpendicular

$$A \rightarrow \qquad \longleftarrow B \quad C \rightarrow$$

parallel

for stretching of the reacting bonds. Bending will be discussed in a later paragraph; it should be included for cases where the activated complex is made nonlinear by, *e.g.*, steric effects.[22] The theory predicts, for substituents at A, that electron supply will make the perpendicular normal vibration shown (A–B bond stretched) more difficult and the parallel normal vibration shown (A–B bond compressed) less difficult. The substituent effect should be determined by the A–B bond, because it is closer to the site of substitution. The perturbation should therefore decrease the normal coordinate corresponding to the perpendicular vibration, *i.e.*, shorten the A–B and B–C bonds (since the force constant is positive), and decrease the normal coordinate corresponding to the parallel vibration, *i.e.*, lengthen the A–B bond and shorten the B–C bond (since the force constant is negative). In a concerted displacement, it is probable that the curvature of the potential energy surface is considerably smaller for parallel than for perpendicular motion;[23] the geometric shift is then expected to be determined largely by the parallel motion (*cf.* eq 3), and the A–B bond should be lengthened while the B–C bond should be shortened by electron supply at A.[24] The same result is (as it should be) predicted for the reverse reaction, *i.e.*, for electron supply to A, which is then the *leaving* group: that the parallel motion ought to lengthen the A–B bond and shorten the B–C bond. For substitution in entering or leaving group, the effects of parallel and perpendicular vibrations are predicted to oppose one another with respect to the bond closest to the substituted group (A–B in the above example) and to reinforce one another with respect to the bond once removed from the substituted group (B–C in the above example). It is not now possible to predict what experimental effect this interesting prediction should have, because the opposed effects occur upon the bond which should inherently be the more sensitive to substituents since it is closer to the site of substitution. It would also be possible to substitute B in the SN2 displacement reaction. In this case electron supply to B should make the perpendicular vibration shown less difficult and have a small effect on the parallel vibration. The effect on the parallel vibration should be small because it should be approximately equal but opposite for the two bonds involved in the parallel normal coordinate (making compression of A–B more difficult and stretching of B–C less difficult). If the reaction were a perfectly symmetric, concerted displacement, A + BA, the parallel effect would be exactly zero by symmetry. The substituent effect should, therefore, be determined by the effect on the perpendicular motion (and is for this reason opposite to Hammond postulate extensions), at least for fairly symmetrical transition states. For nonsymmetrical SN2 transition states, it seems likely, in analogy with Brønsted catalytic effects, that the effect would be greater on the stronger of the A–B and B–C bonds, so that the parallel motion could become important. A theoretical study of the symmetrical and nonsymmetrical cases would be very interesting. The perturbation for the former case of fairly symmetrical transition states should, therefore, increase the normal coordinate corresponding to the perpendicular vibration, *i.e.*, lengthen the A–B and B–C bonds, and this should be the most important substituent effect. This latter effect may be quite small relative to the parallel effects in cases such as substituents at A, because the curvature of the potential energy is likely to be relatively large for perpendicular motion. The predicted pattern of substituent effects is consistent with the experimental data. For example, the chlorine kinetic isotope effect k_{35}/k_{37} for reaction of cyanide ion (1.0060), thiosulfate ion (1.0058), and water (1.0078) with *p*-chlorobenzyl chloride in 80% aqueous dioxane at 30° was found[25] to be largest for the weakest base water. It might be expected that the cyanide isotope effect would be smallest since it is the strongest base; however, this reaction was complicated by concurrent hydrolysis (did not exhibit precisely second-order kinetics) and the isotope effect is, therefore, an average containing some contribution from the high water isotope effect. The solvent isotope effects for CH_3Cl and CH_3Br in H_2O *vs.* D_2O indicate that O–C bond making is more complete for CH_3Cl.[26] This is a case where the substituent change involves an atom of one of the reacting bonds. The prediction for the change from Cl to Br is, in the case of the reactants, that C–X bond stretching will be made easier, *i.e.*, that the C–Br bond will be longer than the C–Cl bond, as is known to be the case

---

(21) *Cf.*, for example, C. G. Swain, R. F. W. Bader, R. M. Esteve, Jr., and R. N. Griffin, *J. Am. Chem. Soc.*, **83**, 1951 (1961).

(22) See C. K. Ingold, *Quart. Rev.* (London), **11**, 1 (1957).

(23) The ratio of curvatures is *ca.* 3–5 for typical surfaces for H_3, which is probably the only three-center transition state for which moderately reliable surfaces are available; see F. S. Klein, A. Persky, and R. E. Weston, Jr., *J. Chem. Phys.*, **41**, 1799 (1964). Also, it should be noted that the success of transition-state theory[3] itself probably rests in part on the relative flatness of the top of the barrier for parallel motion.

(24) If it is true that the H_3 surface really has a shallow basin (*cf.* H. Conroy and B. L. Bruner, *J. Chem. Phys.*, **42**, 4047 (1965)) giving two slightly asymmetric transition states rather than a single symmetrical one, the perpendicular curvature could be considerably weaker than the parallel curvature, which gives a different prediction than the symmetrical case. Study of substituent effects in A + BA displacement reactions might, therefore, provide experimental evidence for the presence or absence of a basin.

(25) J. W. Hill and A. Fry, *J. Am. Chem. Soc.*, **84**, 2763 (1962).

(26) C. G. Swain and E. R. Thornton, *ibid.*, **84**, 822 (1962).

(1.94 *vs.* 1.78 A, respectively). For the transition states, it is predicted that C–X bond stretching will be easier, which implies shorter C–X and longer C–O for methyl bromide resulting from the parallel effect, and longer C–X and C–O resulting from the perpendicular effect. The parallel effect is expected to dominate, so that C–X will be slightly shorter and C–O considerably longer for methyl bromide than for methyl chloride. The transition state is expected to be more reactant-like with respect to C–O for methyl bromide and also more reactant-like for C–Br. The latter prediction was reached by comparison with the rather large substituent effect in the reactant: although C–Br is predicted to be little different in length from C–Cl in the transition state, the reactant C–Br is a great deal longer than the reactant C–Cl, and thus the methyl bromide transition state is a great deal more reactant-like, with respect to the C–Br bond, than the methyl chloride transition state is with respect to the C–Cl bond. The reaction

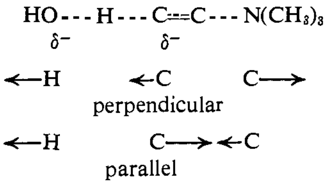
$$N_3^- + ZC_6H_4CH_2S^+(CH_3)_2 \longrightarrow ZC_6H_4CH_2N_3 + CH_3SCH_3$$

appears to have a shorter N–C bond for electron-withdrawing Z, since the solvent sensitivity of the rate of reaction is greater for electron-withdrawing Z (indicating greater charge destruction).[27] With HO^- as the nucleophile instead of N_3^-, the C–S bond is indicated to be shorter for electron-withdrawing Z since the sulfur kinetic isotope effect decreases as Z becomes more electron withdrawing.[28]

Another example is E2 bimolecular elimination. If only the two reacting bonds closest to the substituent are considered (and others are assumed to "follow along"), the effect of substituents Z in the elimination from a species such as β-phenylethyltrimethylammonium ion

$$HO^- + ZC_6H_4CH_2CH_2N^+(CH_3)_3 \longrightarrow H_2O + ZC_6H_4CH{=}CH_2 + N(CH_3)_3$$

should be predictable from the two approximate normal coordinate motions



The true normal coordinates (in particular, that for reaction coordinate motion) will involve more than three atoms, but this merely means that there will be more than one perpendicular motion involving these atoms. A better analysis of such a complex transition state would be arrived at by calculating approximately the true normal coordinates using resonable guesses for the transition-state force constants.[29] The only real necessity in qualitative application of the theory is to separate the reaction coordinate motion from all perpendicular motions, since substituent effects are opposite for positive and negative force constants. In the present approximation it would be predicted that electron-supplying Z would make the perpendicular motion as shown more difficult and make the parallel motion as shown more difficult with respect to the C–H bond and less difficult with respect to the C–C bond. We can expect, however, that in contrast to the SN2 case the effect on the parallel motion will not be zero. The effect on the C–H bond is expected to control the parallel motion because it is a σ bond; the C–C incipient π bond is not expected to change much in this motion because of the presence of the already formed C–C σ bond. It is reasonable to assume that substituent effects will always be larger on σ reacting bonds than on π reacting bonds which are equidistant from the substituent. The perturbation should, therefore, decrease the normal coordinate corresponding to the perpendicular vibration, *i.e.*, shorten the H–C and C–C bonds, and increase the normal coordinate corresponding to the parallel vibration, *i.e.*, lengthen the C–H bond and shorten the C–C bond. If it is assumed that the parallel shift is the more important, the C–H bond should be lengthened and the C–C bond shortened by electron supply at the central C. Since the parallel motion is expected to dominate, and since in this motion compression of the C–C bond is accompanied by extension of the C–N bond, electron supply at the central C is predicted to lengthen slightly the C–N bond. Similarly to the SN2 mechanism, increased electron supply at the base (HO^- in the above example) is predicted to lengthen the O–H bond, *i.e.*, make the transition state more reactant-like, while increased electron supply at the leaving group ($-N^+(CH_3)_3$ in the above example) is predicted to lengthen the C–N bond, *i.e.*, make the transition state more product-like. These predictions are in agreement with the fairly extensive experimental evidence,[30] which is discussed in detail in an accompanying report.[2a]

The SN1 mechanism presents difficulty. The evidence is that in the solvolysis of substituted cumyl chlorides, which presumably proceeds by rate-determining ionization

$$ZC_6H_4C(CH_3)_2Cl \longrightarrow ZC_6H_4C(CH_3)_2^+ + Cl^-$$

the solvolysis rates are more sensitive to solvent polarity (at 25°, methanol, ethanol, 2-propanol) for Z = *m*-methyl- and *p*-phenyl- and less for Z = *p*- or *m*-chloro-, *p*-carbomethoxy-, or *p*-trifluoromethyl- than for Z = H.[31] The data imply that the transition state occurs with more complete ionization for electron-supplying substituents. On the other hand, the present theory predicts that if the reaction coordinate motion is the stretching of the C–Cl bond, electron-supplying Z should make this motion less difficult, *i.e.*, the C–Cl bond shorter at the transition state. It seems likely that the theory is giving a correct prediction and that the sensitivity to solvent polarity (which is very small, barely outside experimental error) does not indicate that electron supply produces a more product-like transition state. One possibility is that the transition state is made more reactant-like in geometry but has more ionic character. There is no reason why geometry and charge separation need parallel one another precisely.[32] The prediction of the present theory is in

---

[27] C. G. Swain, T. Rees, and L. J. Taylor, *J. Org. Chem.*, **28**, 2903 (1963).

[28] C. G. Swain and E. R. Thornton, *ibid.*, **26**, 4808 (1961).

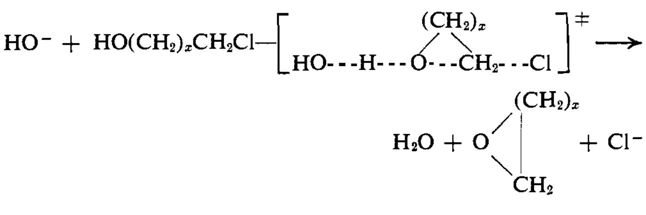
[29] Such calculations are feasible, even for complex molecules, using a computer program such as that developed by J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963); R. G. Snyder and J. H. Schachtschneider, *ibid.*, **21**, 169 (1965).

[30] *Cf.* W. H. Saunders, Jr., in "The Chemistry of Alkenes," S. Patai, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, pp 149–201; L. J. Steffa and E. R. Thornton, *J. Am. Chem. Soc.*, **85**, 2680 (1963).

[31] Y. Okamoto, T. Inukai, and H. C. Brown, *ibid.*, **80**, 4975 (1958).

agreement with that of the Hammond postulate and with intuitive reasoning that the very large rate increases associated with electron-supplying substituents suggest a more reactant-like transition state. The possibility that the direction of the perturbation was predicted incorrectly, *i.e.*, that electron supply actually makes C–Cl bond stretching more difficult, seems unlikely, though some rationalization of such a possibility has been previously given[8] by arguing that reacting bonds are exceedingly electron deficient in the transition state. Electron deficiency of this magnitude now seems very unlikely, and the present theory rejects the possibility by assuming that substituent effects in transition states can be predicted from the same rules which apply to stable molecules. Finally, there is the possibility that the rate-determining step is not simple ionization of the C–Cl bond. An alternative is that the transition state is practically, or even completely, ion-pair-like, with involvement of some nucleophilic center in the rate-determining step.[33] The nucleophile could be solvent or even the π-electrons of the phenyl group (an "internal" nucleophile). The mechanism would then become SN2-like and, if the perpendicular motion were to determine the substituent effect, the C–Cl bond would be predicted to be lengthened by electron-supplying Z. A more detailed discussion of the SN1-type mechanism is in preparation.[2b]

Very little definitive information is available about steric effects upon transition-state structure. It has been shown[17] that the transition state for reaction of hydroxide ion with ethylene chlorohydrin (x = 1) is more product-like than that for tetramethylene chlorohydrin (x = 3).



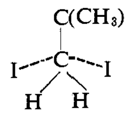
Actually proton transfer to hydroxide ion appears to be complete (prior equilibrium) for ethylene chlorohydrin. The reaction coordinate motion would be approximately

$$\underset{\rightarrow}{\mathrm{O}}\quad\underset{\leftarrow}{\mathrm{C}}\quad\underset{\rightarrow}{\mathrm{Cl}}$$

if the proton transfer were not part of this motion.[17] The ring strain introduced in the compression of the O–C bond is predicted to make the above motion more difficult, giving a more product-like transition state, for the three-membered ring formation. The calculations of steric effects in transition states of SN2 reactions[22] can be understood in terms of perpendicular effects. Larger alkyl groups, in the reaction

$$\mathrm{I^- + RI \rightarrow IR + I^-}$$

were calculated[22] to give longer I–C bonds (both equal by symmetry) at the transition state. In the reaction coordinate motion one I–C bond is compressed while the other is stretched; increased steric size of R should have no effect on this motion. In the perpendicular ICI symmetric stretching motion, compression of both bonds simultaneously should be made more difficult by increased size of R, which should, therefore, make both I–C bonds longer. Also, the calculation showed that the ICI bond angle was bent when R was not symmetric, in a direction away from the bulkiest part of R. For example, if R is neopentyl a 17.6° deviation



from 180° is predicted.[22] The ICI bending motion is a perpendicular motion, so it is predicted that, in comparison with the symmetric case R = CH_3, introduction of one bulky *t*-butyl substituent should make bending of the iodine atoms toward that substituent more difficult and bending away easier, giving a transition state with the I–C–I bonds bent away from the bulky substituent.

Solvation. In making predictions about reactions in solution, one must be concerned about the possibly large effects of the solvent upon the transition state. It cannot be doubted that in many types of reaction mechanism the solvation effect is very large; most ion-forming reactions (*e.g.*, SN2 reactions between uncharged nucleophile and substrate; SN1 reactions) do not proceed in the gas phase, and it can be shown from studies of gas-phase ions that the energy requirements for such reactions are enormous unless very strong stabilization of product ion(s) by solvation occurs. According to the present theory, solvation effects should, if strong, simply make the solvent molecule(s) a part of the transition state.

The theory proposed here assumes that the structure of the unperturbed transition state and the nature of its reaction coordinate are approximately known. It is of fundamental importance, therefore, to provide reliable criteria—experimental and theoretical—for predicting the structures of transition states. The latter is very difficult, especially for reactions involving proton transfer; the position of the proton and the timing of its transfer are difficult to decide because protons tend to be very mobile. "Solvation"[17] and "anthropomorphic"[34] rules have been proposed to help in such predictions. It should be emphasized that these rules apply to the prediction of transition-state structure, which is a completely separate (though related) problem from prediction of substituent effects.

If one accepts the predictive validity of such rules or of the present theory, they can be applied in reverse, *i.e.*, predicted substituent effects can be used to determine transition-state structure or reaction coordinate motion. Such predictions have been used to decide on the mechanism of general acid catalyzed addition of amines[35] and thiols[36] to carbonyl compounds.

It has been suggested[17] that proton transfers between atoms which have unshared pairs of electrons occur rapidly either before or after the transition state, so that the proton "should lie in an entirely stable potential at the transition state and not form reacting bonds nor give rise to primary hydrogen isotope effects."[37]

---

(32) *Cf.* A. Streitwieser, Jr., *Chem. Rev.*, **56**, 638 (1956).

(33) *Cf.* R. A. Sneen and J. W. Larsen, *J. Am. Chem. Soc.*, **88**, 2593 (1966), for direct evidence that attack of solvent on an ion pair can be partly rate determining.

(34) J. E. Reimann and W. P. Jencks, *ibid.*, **88**, 3973 (1966).

(35) C. G. Swain and J. C. Worosz, *Tetrahedron Letters*, 3199 (1965).

(36) G. E. Lienhard and W. P. Jencks, *J. Am. Chem. Soc.*, **88**, 3982 (1966).

(37) *Cf.*, however, R. L. Schowen, H. Jayaraman, L. Kershner, and

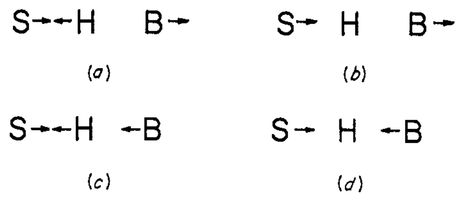


Figure 3. Approximate reaction coordinate motions for extreme types of proton transfer. (a) Concerted, unstable potential; (b) concerted, stable potential; (c) nonconcerted, unstable potential; (d) nonconcerted, stable potential. Note that motion b could not preserve the center of gravity and therefore could not be a normal coordinate for a *triatomic* system, but could be a normal coordinate if other atoms in the transition state also moved in such a way as to keep the center of gravity fixed.

Others have suggested[36] that general acid or general base catalyzed reactions should be thought of as concerted. These superficially conflicting viewpoints actually represent different mechanistic properties: the proton is in an entirely stable potential only if it does not move (relative to the center of gravity of the transition state) in the reaction coordinate motion. The proton may or may not be in a reactant-like or product-like position in the transition state; the determining factor is not the extent of proton transfer, but rather whether the reaction coordinate motion of the transition-state structure, once the transition state is reached, involves or does not involve motion of the proton. If the proton does not move in the reaction coordinate motion, it must move in one or more of the perpendicular motions, *i.e.*, in an entirely stable potential. On the other hand, a concerted, rate-determining proton transfer is one where the proton is actually bonded to a different atom in the first intermediate (or product) on the reaction path after the rate-determining transition state than it was bonded to in the first intermediate (or reactant) on the reaction path before the rate-determining transition state. Though a concerted proton transfer would be expected to involve motion of the proton in the reaction coordinate motion, it is conceivable that the other nuclei could move while the proton did not.

The extreme possibilities are illustrated in Figure 3 for a proton transfer from BH to S.

Extremes b and c seem relatively improbable, but mechanisms approaching these extremes must be considered among the spectrum of possible transition states.

Perturbations According to the Hellmann–Feynman Theorem. The Hellmann–Feynman theorem[38] gives the force acting on any nucleus of a system of electrons and nuclei as the sum of the *classical* repulsions by the other nuclei and attractions by the electrons. It therefore provides a good framework for discussing the qualitative ideas presented in previous sections and may eventually provide a quantitative estimate of perturbations. The force on nucleus α in direction x is given by

$$F_{\alpha x} = \frac{\partial}{\partial x_\alpha} \sum_{(\beta \neq \alpha)} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} - e\int \rho E_{\alpha x} \mathrm{d}\mathbf{r}$$

where Z_α is the nuclear charge of nucleus α, $r_{\alpha\beta}$ the distance between nuclei α and β, e the electronic charge, ρ the total electron density, and $E_{\alpha x}$ the electric field (in the x direction) of nucleus α at the position of the electron, *i.e.*

$$E_{\alpha x} = (Z_\alpha e \cos \theta_\alpha)/r_\alpha^2$$

where θ_α is the angle between a line connecting nucleus α with the electron and the x direction, and r_α is the distance between nucleus α and the electron. The density ρ is given by the sum of the squares of the wave functions for individual electrons, in the one-electron approximation

$$\rho(x,y,z) = \sum_i \psi^*(x_i,y_i,z_i)\psi(x_i,y_i,z_i)$$

By the definition of an equilibrium, all $F_{\alpha x}$ (and $F_{\alpha y}$ and $F_{\alpha z}$) must be zero at the equilibrium geometry of any system, and this includes transition states, where the equilibrium geometry is at the energy maximum, as well as stable molecules, where the equilibrium geometry is at the energy minimum. It is interesting to consider one special case. If two systems, a perturbed and an unperturbed one, both have exactly the same nuclei and differ only in their electron densities ρ, the difference between the forces for the perturbed and unperturbed systems, both forces being evaluated *at the unperturbed equilibrium geometry*, is (since the unperturbed force $F_{\alpha x}{}^{\mathrm{UP}}$ is zero)

$$F_{\alpha x}{}^{\mathrm{P}} = F_{\alpha x}{}^{\mathrm{P}} - F_{\alpha x}{}^{\mathrm{UP}} = -e\int(\rho^{\mathrm{P}} - \rho^{\mathrm{UP}})E_{\alpha x}\mathrm{d}\mathbf{r} = -e\int \Delta\rho E_{\alpha x}\mathrm{d}\mathbf{r} \quad (4)$$

The electric field of the nucleus, $E_{\alpha x}$, is the same for both systems, and the nuclear repulsion part of the force difference exactly cancels since both forces are evaluated at the same geometry. Note that $\Delta\rho$ is a function of three spatial cordinates, not a constant.

The above expression (eq 4) is expected to be a good approximation to the force upon nuclei involved in reacting bonds if a substituent change is made far from the reaction site. In this case the substituent change will change nuclei which are so distant from nucleus α that the nuclear repulsion term will still cancel; $E_{\alpha x}$ of course does not change unless nucleus α is changed. Equation 4 is expected to be a worse approximation in cases where a nucleus close to nucleus α is changed, since the nuclear repulsion terms will change. Also, if nucleus α itself is changed, both the nuclear repulsion terms and $E_{\alpha x}$ will change. However, such an approximation may still be rather good in many cases, if "similar" nuclei replace one another (*e.g.*, chlorine and bromine), because of the fact that inner shell electrons are largely localized around a single nucleus. The inner shell electrons can be thought of as simply shielding the nucleus, *i.e.*, the nuclear repulsion terms and $E_{\alpha x}$ attractions practically cancel for inner shell electrons and the corresponding number of nuclear charges. Approximate calculations can therefore be made using eq 4, but using only the valence-shell electron densities and the (shielded) net valence-shell nuclear charges.

G. W. Zuorick, *J. Am. Chem. Soc.*, **88**, 4008 (1966); J. P. Klinman, Ph.D. Dissertation, University of Pennsylvania, 1966, for evidence that this may not be so in certain cases.

[38] H. Hellmann, "Einfuhrung in die Quantenchemie," Deuticke and Co., Leipzig, 1937; R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939); *cf.* also: J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 932–937; A. C. Hurley, *Proc. Roy. Soc.* (London), **A226**, 170, 179, 193 (1954); **A235**, 224 (1956); T. Berlin, *J. Chem. Phys.*, **19**, 208 (1951); R. F. W. Bader, *Can. J. Chem.* **38**, 2117 (1960); L. Salem and E. B. Wilson, *J. Chem. Phys.* **36**, 3421 (1962).

The very simple electrostatic expression derived for $F^{P}{}_{\alpha x}$ must be summed in order to derive the force for displacement according to normal coordinates, as required in the theory under discussion (*cf.* eq 1 and 2). To simplify notation, let the nuclear coordinates, ***referred to the equilibrium geometry*** x_0, y_0, z_0 for each nucleus, be numbered consecutively, $q_1, q_2, q_3, \ldots q_i \cdots$, where q_1, q_2, q_3 are $(x - x_0)$, $(y - y_0)$, $(z - z_0)$ for nucleus 1; q_4, q_5, q_6 are $(x - x_0)$, $(y - y_0)$, $(z - z_0)$ for nucleus 2; etc. Then the normal coordinates can be written

$$X_j = \sum_i \ell_{ji}{}^{-1} q_i \text{ or } q_i = \sum_j \ell_{ij} X_j \tag{5}$$

For each cartesian coordinate of each nucleus

$$\frac{\partial V}{\partial q_i} \equiv \frac{\partial V}{\partial(x - x_0)} = \frac{\partial V}{\partial x}$$

and

$$F_i = -\frac{\partial V}{\partial q_i} = -\frac{\partial V}{\partial x} = -e\int \Delta\rho E_i \mathrm{dr} \tag{6}$$

as in eq 4. The force for displacement according to normal coordinate X_j is

$$F_{X_j} = -\frac{\partial V}{\partial X_j} = -\sum_i \frac{\partial V}{\partial q_i}\frac{\partial q_i}{\partial X_j} = \sum_i F_i \ell_{ij} = -e\int \Delta\rho(\sum_i E_i \ell_{ij})\mathrm{dr}$$

according to eq 5 and 6. Since all normal coordinates of the unperturbed system are by definition zero at the unperturbed equilibrium geometry, eq 2 gives, for the slope m of the perturbation P (eq 1)

$$m = \frac{\partial V'}{\partial X_j} = -F_{X_j} \tag{7}$$

The assumption of the present theory is that P is linear, *i.e.*, that the slope m does not change much between the unperturbed equilibrium geometry (all X_j zero) and the perturbed equilibrium geometry; if so, eq 7 gives an m applicable to all geometries, not just the unperturbed equilibrium geometry. In fact, eq 7 applies to all geometries since eq 4 gives the difference between the perturbed and unperturbed forces for any nuclear geometry, and (*cf.* eq 2)

$$F_i^{\mathrm{P}} - F_i^{\mathrm{UP}} = -\frac{\partial V^{\mathrm{P}}}{\partial q_i} + \frac{\partial V^{\mathrm{UP}}}{\partial q_i} = -\frac{\partial(V + P)}{\partial q_i} + \frac{\partial V}{\partial q_i} = \frac{\partial P}{\partial q_i}$$

It can then be seen that the quantities F_{X_j} can be defined for any geometry as long as one uses the ℓ_{ij} which apply to an equilibrium geometry (necessary since normal coordinates, and therefore ℓ_{ij}, are not defined except at energy extrema). The net result is that the quantities

$$m = -F_{X_j} = e\int \Delta\rho(\sum_i E_i \ell_{ij})\mathrm{dr} \tag{8}$$

will be constant between the unperturbed equilibrium and perturbed equilibrium geometries if the assumption that the perturbation P is linear is correct, but will otherwise change somewhat.

Equation 8 not only gives a physical picture in terms of an easy-to-visualize quantity, the change in electron probability distribution $\Delta\rho$, but also may provide an approximate means of estimating m values from "classical" electron density approximations, or, better, from approximate wave functions.[39]

A better expression for m can be written in terms of a power series for small displacements from the unperturbed equilibrium geometry ($X_j = 0$)

$$m = (F_{X_j})_{\mathrm{U}} + \left(\frac{\partial F_{X_j}}{\partial X_j}\right)_{\mathrm{U}} X_j + \frac{1}{2}\left(\frac{\partial^2 F_{X_j}}{\partial X^2{}_j}\right)_{\mathrm{U}} X^2{}_j + \ldots \tag{9}$$

where the subscript U means the derivatives are evaluated at the unperturbed equilibrium geometry. Hellmann–Feynman type expressions could be written for the successive terms in eq 9; *e.g.*

$$\frac{\partial F_{X_j}}{\partial X_j} = -e\int \Delta\rho\left(\sum_i \ell^2{}_{ij}\frac{\partial E_i}{\partial q_i}\right)\mathrm{dr}$$

where i is summed over all coordinates of all nuclei.

In a theoretical discussion of substituent effects, it might seem as if the results would be quite different depending upon whether electron density were being supplied to (or withdrawn from) a bonding or an antibonding orbital. It might, therefore, be concluded that such simple ideas as "homonuclear character" and acid–base properties, used in previous sections for predicting substituent effects, would break down in many cases. However, the distinction between bonding and antibonding orbitals is not completely clear-cut, since the usual definition includes nuclear repulsions which are not electron energies at all. In fact, by defining "binding" orbitals as those which, when occupied, produce an attractive force tending to pull nuclei together (even though the nuclear repulsion may more than counterbalance this attractive force), and "antibinding" orbitals as those which produce a force tending to push nuclei apart, Bader and Jones[40] have concluded that essentially all orbitals are binding except at *very* small internuclear distances.

Since the Hellmann–Feynman theorem holds for all geometries of a system of electrons and nuclei, it must hold for transition states. The above arguments show that the primary assumption of the present theory, that transition states can be treated just like ordinary molecules in evaluating substituent effects, is in fact completely correct *if one is calculating effects according to the Hellman–Feynman theorem.* Qualitative arguments concerning the direction of substituent effects are strongly indicated to apply in the same way to transition states as to ordinary molecules, though the validity of such qualitative arguments is not absolutely proven.

From eq 8, it is not immediately obvious why m should be nearly constant with geometry, *i.e.*, why the perturbation should be nearly linear, for it would appear as if E_i, which changes with geometry, must produce large changes in the integral. The reason why such large changes do not occur (at least in diatomic molecules; see following section) is, of course, that $\Delta\rho$ also changes with geometry. Though the individual densities ρ^{UP} and ρ^{P} must probably be redistributed a good deal upon changing the nuclear geometry, it is

---

(39) For an interesting discussion of the hydrogen bond and hydrogen-transfer reactions using simple wave functions with the Hellmann–Feynman theorem, see R. F. W. Bader, *Can. J. Chem.*, **42**, 1822 (1964).

(40) R. F. W. Bader and G. A. Jones, *ibid.*, **39**, 1253 (1961).

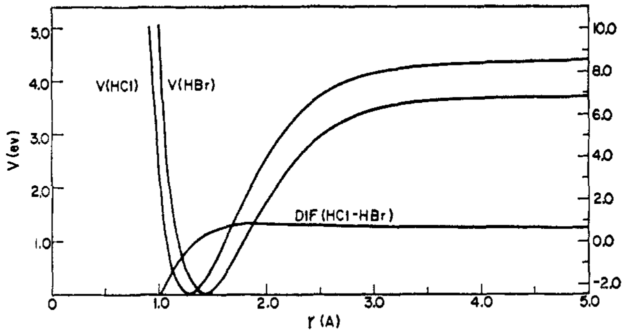


Figure 4. Potential curves for HCl and HBr as calculated from the Hulburt–Hirschfelder equation, along with the difference between the curves (DIF) showing strong curvature of the DIF curve over large changes in *r* (though DIF is very nearly a straight line between 1.2746 and 1.4138 A, the r_e values for HCl and HBr, respectively). It should be noted that the choice of the potential energy scale as zero for each molecule at its r_e affects *only* the vertical placement, and not the shape, of DIF. DIF gives the quantity which, when added to the curve for HBr, gives the curve for HCl.

entirely possible that the electron densities are polarized toward a given nucleus α as it is moved away from other nuclei in nearly the amount required to offset the increased distance of nucleus α by leaving the actual difference distribution $\Delta\rho$ nearly unchanged *relative to nucleus* α. In other words, at least two opposing effects can be expected, which will tend to make *m* constant with geometry (for small changes in geometry).

Substituent Changes in Diatomic Molecules. In order to investigate the validity of the assumption that perturbations are linear, the actual differences between potential energy curves for some diatomic molecules have been calculated and these differences checked for linearity. A computer program[41] has been written which calculates the energy of a diatomic molecule for interatomic distances from 0 to 5 A at 0.1-A intervals, and at 0.02-A intervals between any specified pair of interatomic distances, from the potential function of Hulburt and Hirschfelder.[42] The experimental parameters ω_e, $\omega_e x_e$, D_e, B_e, α_e, and r_e, along with the reduced mass, are used to give a (supposedly) rather good prediction of the potential energy curve. The program then calculates the energy differences between all possible pairs (up to eight molecules may be examined in one computation) of molecules at the above geometries and computes the slope, intercept, and standard deviation of points for the best straight line through only the differences taken at 0.02-A intervals. Also, the program gives the differences, calculated according to the above best straight line, for all geometries from 0 to 5 A, along with the differences between the experimental and calculated differences.

Calculations have been made for H_2, H_2^+, HCl, HCl^+, HBr, HI, and CH, from which some tentative conclusions can be drawn. The spectroscopic constants from Herzberg's table[42b] were used.

The differences are reasonably linear but tend to be concave upward, as mentioned in a previous section. These differences must, physically, approach (probably asymptotically) constant values as the internuclear distance approaches infinity (separated atoms) and (*not* counting nuclear repulsions) zero (combined atoms). The former is reproduced by the program; the equation does not give correct energy results as the distance approaches zero anyway.[42]

The differences are precisely linear for molecules with the same nuclei, *i.e.*, H_2 *vs.* H_2^+ and HCl *vs.* HCl^+. For example, the slope for HCl minus HCl^+ is 1.129 ev A^{-1}, and the standard deviation of points from the line (1.10 to 1.62 A) is 0.004 ev (the equilibrium internuclear distances are 1.27 and 1.31 A, respectively). For H_2 minus H_2^+, the slope is 5.799 ev A^{-1}, and the standard deviation (0.74 to 1.06 A) is 0.035 ev (equilibrium internuclear distances 0.74166 and 1.060 A, respectively). This discovery indicates that, for merely electronic changes, without change of nuclei, the perturbations considered for substituent effects ought to be precisely linear. For complex molecules where the substituent change is made relatively far from any reacting bonds, the only effect on the reaction center should be a small change in electron density, which can be expected to produce perturbations that are much more nearly linear than the change from HCl to HCl^+.

The differences are considerably less linear for molecules of different types. For example (a particularly bad case), the slope for HI minus CH is -15.17 ev A^{-1}, and the standard deviation (1.10 to 1.62 A) is 0.85 ev (equilibrium internuclear distances 1.60 and 1.12 A, respectively). The slope changes from 46.5 to 3.5 ev A^{-1} between 1.10 and 1.62 A. This is a case where the equilibrium nuclear distances are quite different, and it can be expected that such drastic changes of "substituent" will be likely to produce large deviations from linearity. A case more typical of the type of closely related structures that might be compared experimentally is HCl minus HBr (*e.g.*, where Cl and Br are compared as leaving groups), giving: slope, 4.131 ev A^{-1} (1.10 to 1.62 A), standard deviation, 0.17 ev; equilibrium internuclear distances, 1.27, 1.41 A. The computer-calculated curves for HCl and HBr, along with their difference curve, are plotted in Figure 4.

Linearity is much better for the latter pair if the data between 1.26 and 1.40 A are used (*i.e.*, approximately between the equilibrium internuclear distances): slope, 4.238 ev A^{-1}; standard deviation, 0.016 ev. Furthermore, in cases where one of the atoms of a reacting bond is changed, transition-state perturbations must be considered relative to rather large reactant perturbations. In principle, the deviations from linearity would be expected to be of similar magnitude for reactant and transition state, and would, therefore, tend to cancel in considering, *e.g.*, changes in reactant-like *vs.* product-like character in transition states.

Of course, another possible source of nonlinearity is the approximate nature of the Hulburt–Hirschfelder equation,[42] since the differences are taken at points fairly far removed from the equilibrium internuclear distance of at least one of each pair of molecules. The calculated energies for H_2 agree with the "most likely" values from vibrational energy level analysis[43] to within *ca.* ±0.01 ev between 0.5 and 1.4 A, but at larger internuclear distances, agreement becomes worse:

---

[41] Written in FORTRAN IV for the IBM 7040 computer of the University of Pennsylvania Computer Center.

[42] (a) H. M. Hulburt and J. O. Hirschfelder, *J. Chem. Phys.*, **9**, 61 (1941); note an error of sign in the definition of the parameter *b*, where the first plus sign should be a minus sign. (b) This error is also reproduced in G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Company, Inc., Princeton, N. J., 1950, p 102.

[43] D. Steele, E. R. Lippincott, and J. T. Vanderslice, *Rev. Mod. Phys.*, **34**, 239 (1962).

e.g., 0.12 ev at 2.0 A. The energies from the Hulburt–Hirschfelder equation have been compared with the energies from precise vibrational analysis for a series of 19 electronic states of several diatomic molecules,[43] and the average per cent difference between these energies relative to the dissociation energy, $(V_{\text{H-H}} - V_{\text{VA}})/D_e$, is only about 1.5%, over the entire range of geometries for which vibrational data are available for all the molecules studied. Additional complications might conceivably arise from irregularities in potential energy curves, *e.g.*, if there is configuration interaction with low-lying excited states;[44] even in this case, however, the effects might be expected to cancel in considering the difference between unsubstituted and substituted molecules or transition states, provided the substituent change is not too drastic.

The linearity of the difference between species containing the same nuclei is surprisingly precise,[45] and should be further explored, especially in relation to the Hellmann–Feynman theorem (*e.g.*, eq 4).

Problems of Theory. The major problem in applying this theory qualitatively to large organic molecules is choosing the reaction coordinate. It would be highly desirable to have "rules" (*cf.* ref 17 and 34) to aid in predicting the correct reaction coordinate.

Curvature of the perturbation could be a problem, but the results with diatomics indicate that, for "small" substituent changes, large curvature is unlikely. Also, this problem's existence could be investigated by studying several substituents in the same reaction; if the results fell in a rational order dependent on electronic or steric properties of the substituents, large curvature, or at least reversal of slope, could be ruled out.

For qualitative predictions, it is difficult to decide precisely about effects which may nearly cancel, *i.e.*, where opposite effects on the same bond are predicted from two different normal vibrations. Associated with this problem is the question whether (or when) it is justifiable to assume that the curvature of the potential energy surface in the reaction coordinate (parallel) direction is considerably less than in the perpendicular directions.

Interpretation of experiments is another type of difficulty. It is not easy to design experiments which unambiguously indicate whether a certain bond is lengthened or shortened, in the transition state, by a substituent change. Solvation effects must be considered as well as effects associated with ordinary bonds. This problem is especially important in the case of the SN1 mechanism, which will be an important test for this theory.

Conclusion. The theory appears to give reliable qualitative predictions based on an approximate knowledge of the reaction coordinate for a reaction. It can be understood theoretically in terms of the Hellmann–Feynman theorem, and it seems justified on various qualitative grounds. We hope to explore the idea further by trying to refine the qualitative predictions (including study of substituent effects on molecular vibrations), further justify it and make quantitative predictions, and carry out experimental tests designed to uncover and explain any exceptions that may exist.

Acknowledgment. The author is grateful to Professors C. G. Swain and R. L. Schowen for helpful discussions.

---

(44) R. S. Mulliken, *J. Am. Chem. Soc.*, **88**, 1849 (1966).

(45) It tends to justify the approach to excited-state geometry previously mentioned (Malrieu[12]).