The Principle of Least Motion. Application to Reactions of Resonance-Stabilized Species[1a]

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According to Rice and Teller's principle of least motion and similar statements by other workers, those elementary reactions will be favored that involve the least change in atomic position and electronic configuration. Using methods pioneered by Polanyi, Bell, and their co-workers it is estimated that in the protonation of the cyclohexadienyl anion, the necessity for greater changes in internal geometry may cause the activation energy for the formation of 1,3-cyclohexadiene to be larger than that for the formation of 1,4-cyclohexadiene by 0.5–1.0 kcal/mole or more. Thus the principle of least motion leads to an effect that is in the proper direction to explain the more rapid formation of the less stable isomer and that is large enough to be of significance in such an explanation. The principle is applied, by use of a more qualitative method, in a discussion of the position of reaction of mesomeric carbonium ions, carbanions, and radicals. According to the principle there should be a tendency for pentadienyl and cinnamyl intermediates to yield more of a less stable, less conjugated product but for benzyl intermediates to yield more of the more stable (benzyl) products. Other factors of possible importance in determining the position of preferential reaction of mesomeric species are also considered. Also discussed is a tendency for aliphatic nitro compounds to form carbanions more slowly than equally or less acidic compounds whose transformations to carbanions are accompanied by smaller changes in molecular geometry, a tendency for imidazoles to remove protons more slowly than pyridines of equal basicity, and other rate-equilibrium disparities.

As Hückel,[2] Wheland,[3] and others have pointed out, the use of chemical reactions to deduce the structure of organic compounds is based on the (generally tacit) assumption that the *principle of minimum structural change* is usually applicable. From this principle it is a relatively short step to such generalizations as Muller's *principle of least molecular deformation*, according to which the atomic linkages change as little as possible during a reaction.[4,5]

In discussing the role of free radicals in elementary organic reactions, Rice and Teller enunciated the *principle of least motion.*[6] According to this principle, *those elementary reactions will be favored that involve the least change in atomic position and electronic configuration.* As Rice and Teller pointed out, similar statements had been made by Franck and Rabinowitsch[7] and the principle is implicit in the approach of Eyring and co-workers to reaction rate theory.[8,9] There are a number of observations, including certain apparent anomalies, concerning the effect of structure on reactivity that seem at least qualitatively explicable in terms of the principle. One relevant set of data consists of the existing observations on rates and orientation in the reactions of resonance-stabilized species. Quite commonly in closely related one-step reactions, the reaction with the larger equilibrium constant also has the larger rate constant. Evidently the two transition states bear enough resemblance to the products to reflect their relative stabilities. In a considerable number of other cases, however, including a number of reactions of resonance-stabilized species, it is the reaction with the smaller equilibrium constant that has the larger rate constant; *e.g.*, a reactive intermediate gives the less stable of two isomeric products more rapidly than it gives the more stable one.[10a] Consideration of the nature of many of these cases reveals that the difference in molecular structure between reactants and products is smaller for the more rapidly formed product than for the less rapidly formed product. In discussing the formation of resonance-stabilized anions, Bell pointed out that reactions tend to be slow "for systems involving a large structural change on ionization," but he gave an electrostatic explanation for this fact.[11] In regard to the same subject, Dewar stated, "the entropy of activation will be least for the reaction which leads to least displacement of nuclei," and in another connection, "Reaction ...should then occur more readily...since a smaller movement of groups will be required and the activation energy will therefore be less."[12]

In the present discussion the principle of least motion will be applied to the reactions of resonance-stabilized species in a manner that will permit, in at least some instances, a semiquantitative estimate of the order of magnitude of the effect.

Discussion

The Basis for the Principle of Least Motion.—The present discussion will be based on the method of Polanyi and co-workers for treating the rates of atom-transfer reactions,[13,14] a method that in turn followed

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(1) (a) Part X in the series, Polar Effects on Rates and Equilibria. Part IX: J. Hine and R. D. Weimar, Jr., *J. Am. Chem. Soc.*, **87**, 3387 (1965). This work was supported by Research Grant AM 06829 MCB from the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, U. S. Public Health Service, and Grant GP-4445 from the National Science Foundation. It was described preliminarily in a Kelley Lecture at Purdue University in May 1964. (b) Evans Chemistry Laboratory, The Ohio State University.

(2) W. Hückel, "Theoretische Grundlagen der Organischen Chemie," 2nd ed, Akademische Verlagsgesellschaft M.B.H., Leipzig, 1934, pp 139–142.

(3) G. W. Wheland, "Advanced Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, Section 2.3.

(4) J.-A. Muller, *Bull. Soc. Chim. France*, **45**, 438 (1886).

(5) J.-A. Muller and E. Peytral, *Compt. Rend.*, **179**, 831 (1924), and references cited therein.

(6) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939).

(7) J. Franck and E. Rabinowitsch, *Z. Elektrochem.*, **36**, 794 (1930).

(8) A. Sherman and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932).

(9) G. E. Kimball and H. Eyring, *ibid.*, **54**, 3876 (1932).

(10) *Cf.* J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962: (a) Section 10-2c; (b) Section 5-3b; (c) Section 1-1b; (d) Section 10-1c.

(11) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter X.

(12) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp 104, 144.

(13) R. A. Ogg, Jr., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 604, 1375 (1935).

(14) M. G. Evans and M. Polanyi, *ibid.*, **34**, 11 (1938).

from the earlier treatment of certain atom-transfer reactions by Eyring and Polanyi[15] using techniques devised by London.[16] This method was applied to proton-transfer reactions by Horiuti and Polanyi[17] and such applications have been considered in detail by Bell and co-workers.[11,18–20] These applications have added greatly to our understanding of the effect of structure on reactivity; they have, for example, permitted a rationalization of the Brønsted catalysis equation and the change in the magnitudes of Brønsted α and β values that accompany changes in reactant structures.[10b,11,17–20]

For a reaction of the type 1, the method involves estimating the potential energy of the system as a function of a geometric coordinate that is a measure of the extent to which Y has been transferred from X to Z. The estimates are based on potential energy curves for stretching the XY and YZ bonds and on allowance for resonance stabilization.

$$\mathrm{XY} + \mathrm{Z} \longrightarrow \mathrm{X} + \mathrm{YZ} \qquad (1)$$

A number of treatments of resonance have been carried out by closely analogous methods except that the reactions treated are not ordinarily single-atom transfers but isomerization reactions.[10c,21–25] In these cases one constructs two curves representing changes in the *total* energy to be expected for the two different valence-bond structures as a function of the geometric configuration rather than just the energy required to stretch one bond. In such treatments it has been pointed out qualitatively that, if the optimum arrangement of the atomic nuclei for one valence-bond structure differs greatly from the optimum arrangement for the second valence-bond structure, the two different valence-bond structures will correspond to two different kinds of molecules separated by a large energy barrier. When the expected geometric differences between the two valence-bond structures are smaller, the energy barrier between the two different kinds of molecules is smaller, and, when the expected molecular geometries are similar enough, only one kind of molecule, a resonance hybrid of the two valence-bond structures, is found to exist. In certain cases, such as those in which vertical resonance energies were estimated, the amount of energy required for internal molecular distortion has also been estimated quantitatively, largely from bond-stretching force constants.[22–25]

In the present treatment Y will be assumed to remain collinear with X and Z; it will be sufficient to define the reaction coordinate g so that the value zero corresponds to the geometry of the reactants, with Y fully bonded to X, and the value 1.0 corresponds to the geometry of the products, with Y fully bonded to Z.

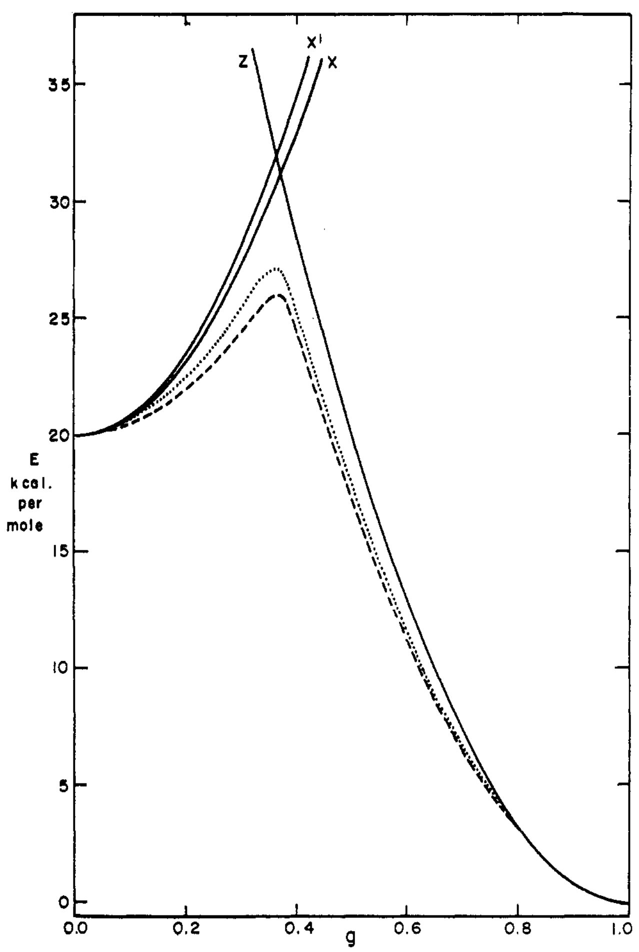

Figure 1.—Plot of potential energy (E) *vs.* the geometric coordinate (g).

Although changes in g will indicate largely movement of Y, this movement will be acccompanied by small changes in the X–Z distance; this latter distance may be defined as that which corresponds to the lowest potential energy for the given extent of transfer of Y. The potential energy of the system, as a function of the coordinate g, will be estimated by constructing curve x, representing the potential energy to be expected of the system if it is considered to consist of XY and Z with no interaction between the two, and the curve z, corresponding similarly to the valence-bond structures X and YZ. Thus, at a g value of zero curve x represents the potential energy that the species XY and Z would have in their optimum geometric configurations if they were far enough apart not to interact with each other. At a g value of 1.0 curve x represents the potential energy of an XY molecule (or ion) in which the X–Y bond has been greatly stretched and in which the geometry of the X part of the species has been changed (if any change is needed) to that characteristic of free X plus the potential energy of a Z whose internal geometry has been changed (if necessary) to that characteristic of the Z part of a YZ molecule in its most stable configuration. From the definition of g, curve x has a minimum at zero and curve z has a minimum at 1.0, as shown in Figure 1. According to Figure 1 (which corresponds to a reaction in which the products are 20 kcal/mole more

(15) H. Eyring and M. Polanyi, *Z. Physik. Chem.*, **B12**, 279 (1931).

(16) F. London, "Probleme der modernen Physik," Sommerfeld-Festschrift, S. Hirzel, Leipzig, 1928, p 104; *Z. Elektrochem.*, **35**, 552 (1929).

(17) J. Horiuti and M. Polanyi, *Acta Physicochim. URSS*, **11**, 505 (1935).

(18) R. P. Bell, *Proc. Roy. Soc.* (London), **A154**, 414 (1936).

(19) R. P. Bell and O. M. Lidwell, *ibid.*, **A176**, 114 (1940).

(20) R. P. Bell, "Acid–Base Catalysis," Oxford University Press, London, 1941, pp 160–175.

(21) G. E. K. Branch and M. Galvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1941, p 74.

(22) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, Sections 1-4 and 3-7.

(23) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(24) D. F. Hornig, *ibid.*, **72**, 5772 (1950).

(25) C. A. Coulson and S. L. Altmann, *Trans. Faraday Soc.*, **48**, 293 (1952).

stable than the reactants), as Y moves away from X the potential energy of the system increases along curve x until the point of intersection with curve z; after this point the system is better described as X + YZ and the energy decreases along curve z. For an improved approximation, it is necessary to allow for interaction between XY and Z (or X and YZ). The most important interaction will be resonance stabilization owing to the simultaneous contribution of all three types of valence-bond structures

$$\underset{\text{I}}{\text{X—Y Z}} \longleftrightarrow \underset{\text{II}}{\text{X Y Z}} \longleftrightarrow \underset{\text{III}}{\text{X Y—Z}}$$

Curve x includes an allowance for the two structures on the left and curve z includes an allowance for the two structures on the right, but allowance for all three structures simultaneously leads to increased resonance stabilization, which should be at a maximum near the point at which curves x and z cross, since at this point the energy content to be expected of the first and third structures will be nearly equal. The dashed line in Figure 1 represents the type of potential energy curve that could result when such interaction is taken into account.

In a simple treatment, curves x and z may be calculated by consideration of the energy required to stretch the X–Y and Y–Z bonds. The shape of such curves, near their minima at least, may be obtained from stretching force constants derived from spectral data. Such force constants depend on the nature and hybridization of the two atoms bonded but are relatively independent of changes in structure elsewhere in the molecule.[26] This treatment should be applicable to cases in which X and Z are groups whose internal geometry is unaffected by attachment to Y, in addition to cases in which X and Z are monoatomic. However, in cases in which the internal geometry of X or Z changes significantly upon bonding to Y, such geometric changes must be taken into account.

Let us assume that reaction 1 is a process in which no internal changes in geometry occur and that curves x and z in Figure 1 are appropriate for this reaction. Now let us consider the related reaction 2, involving

$$\text{XY} + \text{Z}' \longrightarrow \text{X} + \text{YZ}' \qquad (2)$$

the same over-all potential energy change, in which the internal geometries of X and Y do not change during the reaction but the internal geometry of Z′ does. In curve x the energy increases on going to the right because of the stretching of the X–Y bond. In the present case the internal geometry of Z′ is also being changed and therefore it will be necessary to add to curve x an increment equal to the energy required for this change. Addition of this increment, which may be estimated from the magnitude of the over-all change in the geometry of Z′, the relevant force constants, and some assumption about the manner in which the internal geometric change is correlated with g, gives curve x'.

Thus, if no correction is made for resonance stabilization, the transition state for reaction 2 is estimated to lie at the intersection of curves x' and z, which is higher than the intersection of curves x and z, the estimated transition state for reaction 1. Less resonance stabilization would be expected for the transition state in reaction 2 than for the transition state in reaction 1. Resonance stabilization of the transition state in reaction 2 is diminished not only by the fact that the actual X–Y and Y–Z bond distances are not the optimum distances for contributing valence-bond structures like I and III (a factor that is also important in reaction 1) but also by the fact that the internal structure of Z′ is not optimum for any of the three contributing structures. The dashed curve in Figure 1 may be taken to represent the potential energy curve for reaction 1 when correction for resonance stabilization has been made. The corrected curve for reaction 2 may then be represented by the dotted line, whose maximum lies below the intersection of curves x' and z by an amount (the resonance stabilization of the transition state) that is smaller than the amount by which the maximum for the dashed curve lies below the intersection of curves x and z.

It may be argued that the simultaneous occurrence of changes in the internal geometry of Z should make the transfer of Y easier or they would not occur (on the path of lowest energy requirement). This is true in the sense that, in a system in which the internal geometry of Z′ is much different in YZ′ from what it is in free Z′, if Y is transferred to Z′ without simultaneous changes in the internal geometry of Z′, a higher energy barrier would be expected than if the internal geometric changes did occur. This is true because the reaction products would no longer be X + YZ′ but X + YZ*; that is, YZ′ would not be formed in its most stable geometric configuration but in a less stable geometrically distorted excited state. Nevertheless, the previous argument shows that, if the reaction of XY with Z′ is compared with a reaction having the same equilibrium constant but smaller concomitant changes in internal geometry, the former reaction will be slower.[27] More generally, of two closely related one-step reactions, the one involving smaller changes in molecular geometry will tend to be faster. From the treatment employed it also follows that the one giving the more stable product will tend to be faster. These two tendencies may work together or they may be opposed.

Semiquantitative Application of the Principle of Least Motion.—Before attempting qualitative applications of the principle of least motion to the explanation of various reactivity anomolies, it should be useful to learn whether changes in internal molecular geometry of the magnitude commonly encountered in reactions would be expected to produce rate effects large enough to be of significance in explaining such anomalies. A really quantitative evaluation of such effects requires data that are not available and complicated calculations, but the probable order of magnitude may be estimated by use of various approximations. Such an estimate will be made for the case of the protonation of the cyclohexadienyl anion by an alcohol molecule.

An unreliable but not entirely arbitrary estimate of the energy change accompanying the protonation of

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[26] G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 192.

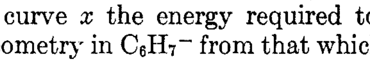
[27] Curves x, x', and z were not constructed to give qualitative agreement with the statements in the present section; they were plotted from the equations described in the following section so as to be applicable to a specific reaction, the protonation of a cyclohexadienyl anion to give 1,4-cyclohexadiene.

cyclohexadienyl anions by alcohol molecules was begun by noting that upon treatment with ethanolic potassium ethoxide, triphenylmethane forms carbanions somewhat slower, but indene, fluorene, and acetophenone form them much faster,[28] than does 1,4-cyclohexadiene[29] upon treatment with potassium *t*-amyloxide. The difference in reactivity of 1,4-cyclohexadiene and triphenylmethane was then attributed to differences in reaction conditions and 1,4-cyclohexadiene was assigned the pK value (33) that has been suggested for triphenylmethane.[30] This value differs from that assigned to alcohols by 14–17 units,[30] corresponding to a free-energy difference of about 20 kcal/mole. Therefore, in Figure 1, the minimum for curve x is constructed 20 kcal above that for curve z. Since there are uncertainties regarding the shapes of the basic energy curves[13,14,17–20] and since the shapes of the curves have no appreciable effect on the magnitude of the calculated effect except insofar as they affect the g value at which the two curves intersect, for the sake of simplicity we have chosen two congruent parabolas to depict curves x and z. Curve x represents the energy that would be expected for the system considered as ROH + $C_6H_7^-$ (with no interaction between the two species) as g is changed from 0 (optimum geometry for the system) to 1.0 (geometry optimum for RO^- + 1,4-cyclohexadiene) if it were not necessary to change the internal geometry of the $C_6H_7^-$ group. Curve z represents the energy that would be expected for RO^- + 1,4-cyclohexadiene (with no interaction between the two) as g changes from 1.0 to 0, *i.e.*, as the carbon–hydrogen bond in question is stretched. The relative positions of the minima for the parabolas having been set, as have the locations of their axes at g values of 0 and 1.0, the only remaining parameter (the curvature of the parabolas) was chosen so that activation energies near the experimental values[29] will be obtained. The resulting equation for x is

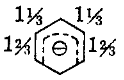
$$E = 20 + 80g^2$$

In applying the principle of least motion, curve x' is defined as describing the total energy to be expected of ROH + $C_6H_7^-$ (with no interaction) at various g values. To obtain curve x' we must, at every value of g, add to curve x the energy required to change the internal geometry in $C_6H_7^-$ from that which is optimum for the carbanion to that which is characteristic of the given g value. The geometry characteristic of a g value of 0 is that optimum for $C_6H_7^-$, so that curves x and x' coincide at this point; at a g value of 1.0 the characteristic geometry for the $C_6H_7^-$ part is that which is optimum for the $C_6H_7^-$ part of 1,4-cyclohexadiene, and at all g values between 0 and 1.0 the characteristic geometry is intermediate between these extremes.

The cyclohexadienyl anion may be represented by a simple resonance treatment in terms of the three equally contributing structures IV–VI. Pauling's method of calculating bond numbers[31] leads to the following values.



IV V VI



VII

Bastiansen and Traetteberg's single-bond radii of 0.737 and 0.767 A for sp^2 and sp^3 carbon and a double-bond radius of 0.669 A[32] were used to calculate the lengths of single and double bonds in the cyclohexadienes and the cyclohexadienyl anion. For bonds of fractional number, lengths were read from a smooth curve drawn through the values 1.474 and 1.338 A thus obtained for sp^2 single and double bonds, and values of 1.420 (graphite)[31] and 1.397 A (benzene)[31] representing $1^1/_3$ and $1^1/_2$ bonds.[33] Force constants for various bonds were estimated by using Badger's rule.[31,34] These correlations lead to the bond lengths and force constants shown in Table I.

TABLE I
BOND LENGTHS AND FORCE CONSTANTS USED IN CALCULATIONS

Type of bond	Length, A	Force constant, dynes/cm
Double	1.338	984,000
$1^2/_3$	1.376	826,000
$1^1/_3$	1.420	685,000
sp^2–sp^2 single	1.474	557,000
sp^2–sp^3 single	1.504	501,000
sp^3–sp^3 single	1.534	457,000

Assuming that geometric changes are a linear function of the geometric coordinate g, curve x' is determined by adding to curve x the following function of g (eq 3), based on Hooke's law, where 143.9 is a conversion factor to give the units shown.

$$\Delta E_{x'} = {}^1/_2[2(8.26)(1.376 - 1.338)^2 + 2(6.85)(1.504 - 1.420)^2]143.9g^2 \text{ kcal/mole} \quad (3)$$

As shown in Figure 1, curve x' intersects curve z at a point 0.74 kcal/mole higher than curve x does.[36] According to the argument given in the previous section, this is an estimate of the amount by which the necessity for change in internal geometry increases the activation energy of the reaction. All that we hope to be able to compare with experimental observations in the present case, however, is the *difference* between the effects on the rates of formation of 1,4- and 1,3-cyclohexadiene.

For this purpose we use curve x'' (omitted from Figure 1 to avoid cluttering), which corresponds to

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[28] (a) A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 163 (1963); (b) *ibid.*, **1**, 196 (1963).

[29] R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3032 (1963).

[30] W. K. McEwen, *ibid.*, **58**, 1124 (1936).

[31] L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 231–238.

[32] O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962).

[33] For our purposes this has an advantage over Pauling's similar correlation[31] in that it gives a plausible value for the sp^2–sp^2 single bond in a conjugated diene without having to assign fractional character to the bond. From the curve the bond lengths of naphthalene and anthracene may be calculated with an average deviation (0.005 A), slightly less than that obtained using Pauling's correlation.

[34] According to this rule a plot of $k^{-1/3}$ (where k is the force constant) *vs.* the bond length should give a straight line. Carbon–carbon stretching force constants for ethylene, benzene, and ethane[35] and bond distances of 1.338, 1.397, and 1.534 A were used in an appropriate plot.

[35] J. W. Linnett, *Quart. Rev.* (London), **1**, 73 (1947).

[36] It is more convenient to determine the points of intersection analytically than graphically.

the energy changes to be expected of ROH + $C_6H_7^-$ when its geometry is changed to that which is optimum for RO^- + 1,3-cyclohexadiene. This curve is obtained by adding to curve x the function shown in eq 4.

$$\Delta E_{x''} = {}^1/_2[8.26(1.376 - 1.338)^2 + 6.85(1.474 - 1.420)^2 + 6.85(1.420 - 1.338)^2 + 8.26(1.504 - 1.376)^2 + 5.01(1.534 - 1.504)^2]143.9g^2 \text{ kcal/mole} \quad (4)$$

The transition state should not occur at the intersection of curve x'' with curve z, which refers to 1,4-cyclohexadiene, but with a curve congruent to z and 0.07 kcal/mole lower, since 1,3-cyclohexadiene is 0.07 kcal/mole more stable than the 1,4 isomer (after correction for differences in symmetry numbers).[29] The intersection of this latter curve with curve x'' occurs at a point 1.27 kcal/mole higher than the intersection of curves x and z and hence 0.53 kcal/mole higher than the intersection of x' and z. Thus the activation energy for 1,4-cyclohexadiene formation is estimated to be lower than that for 1,3-cyclohexadiene formation by at least 0.53 kcal/mole. The estimated difference in activation energies would be larger if resonance stabilization were taken into account. If the assumption that internal movements in the cyclohexadienyl groups are a linear function of g is true, then at any g value the system in which 1,3-cyclohexadiene is being formed differs more, geometrically, from a cyclohexadienyl anion and from the diene being formed than does the system in which 1,4-cyclohexadiene is being formed.

In view of the uncertainties in the estimate of 20 kcal/mole for the energy of reaction, it should be pointed out immediately that the magnitude of the calculated effect is dependent on the value chosen for the energy of reaction. When the absolute magnitude of the energy of reaction is so large that the two curves intersect at a g value near 0 or 1.0, the geometric change effect is relatively small. The geometric change effect reaches a maximum when the energy of reaction is such that the two curves intersect at a g value near $^2/_3$.[37] In this case the activation energy for the formation of the 1,4-diene is estimated to be lower by more than 0.9 kcal/mole.

The values calculated here for the geometric change effect would be larger if certain other methods for estimating the structure of the cyclohexadienyl anion were used.[38]

Bates, Carnighan, and Staples' results[29] correspond to a difference in free energies of activation of 1.5 kcal/mole and the preliminary results of Doering and coworkers[40] to a difference of about 4.3 kcal/mole (both values statistically corrected).

Although the method of estimation used in the present paper is too crude for the exact differences in activation energy to have much significance, the principle of least motion has been shown to lead to an effect that operates in the proper direction and is of an order of magnitude adequate to contribute significantly toward explaining the experimental results.

Some of the factors that have been neglected, such as changes in carbon–hydrogen bond lengths owing to changes in the hydridization of carbon, should be essentially the same for the formation of the two olefins and therefore would not contribute significantly to the *difference* in activation energies calculated. Other factors, such as changes in bond angles, etc., cannot be estimated very reliably without better information concerning the exact structure and vibrational force constants for the two dienes and their conjugate base. Partly for this reason, the use of the same x curves (before addition to the ΔE terms) and congruent z curves for 1,3- and 1,4-cyclohexadiene is perhaps the major approximation made in the treatment described.

Qualitative Application of the Principle of Least Motion.—Since the correlation of bond lengths with bond numbers used in the previous section may be represented by a straight line without introducing an error of so much as 0.005 A, the energy required to bring about internal geometric changes, which is proportional to the squares of the magnitudes of the individual changes, should be approximately proportional to the sum of the squares of the changes in bond numbers. Thus if the cyclohexadienyl anion is represented by hybrid structure VII, protonation to give 1,4-cyclohexadiene involves the transformation of two $1^1/_3$ bonds to single bonds and two $1^2/_3$ bonds to double bonds, the sum of the squares of the changes in bond numbers being $^4/_9$. Protonation to give 1,3-cyclohexadiene involves one each of the following changes in bond number: $1^2/_3$ to 2, $1^1/_3$ to 1, $1^1/_3$ to 2, and $1^2/_3$ to 1, the sum of the squares of the changes being $^{10}/_9$. Therefore, the principle of least motion should favor the formation of 1,4-cyclohexadiene.

In the cases of simple linear pentadienyl anions an essentially identical evaluation shows that the principle of least motion would again favor the formation of the unconjugated diene. The conjugated diene will usually be more stable than the unconjugated diene to a greater extent than in the case of the cyclohexadienes. This extra stability will tend to increase the rate of formation of the conjugated diene; it corresponds to a lowering of the z curves relating to the formation of the more stable isomer relative to the other z curves.

If the product stability effect is large enough it would be expected to be the controlling effect. Since the geometric change effect reaches a maximum at an intermediate value of g and decreases as g approaches either 1.0 or 0, whereas the product stability effect increases steadily as g increases from 0 to 1.0, product stability is more likely to be the controlling factor in cases where the transition state comes late in the reaction, that is, in cases where the reaction products (*e.g.*, reactive intermediates) are considerably less stable than the reactants.

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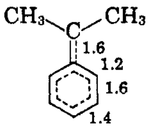
(37) This and certain other statements apply to cases in which the two basic parabolas are congruent or nearly congruent. In some real cases the two curves may be so dissimilar that the discussion given would have to be modified slightly.

(38) To paraphrase Zimmerman's discussion,[39] hybrid structure VII arises as a first approximation by assuming equal contributions of structures IV, V, and VI; in subsequent approximations structure V would be weighted more heavily than IV or VI since it corresponds to a geometric configuration that is closer to that of the actual hybrid. Such an increase in the weight assigned structure V would lead to an estimated hybrid structure whose carbon–carbon bond distances are more nearly equal to those in 1,4-cyclohexadiene and less like those in 1,3-cyclohexadiene than are those in VII. Using bond numbers of 1.316 and 1.684 derived from Zimmerman's charge densities, the estimated differences in activation energies are slightly more than 10% larger than those calculated above.

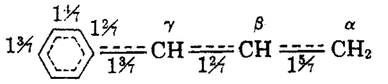
(39) H. E. Zimmerman, "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 348.

(40) W. v. E. Doering, G. Schroeder, K. Trautner, and S. Staley, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p 14M.

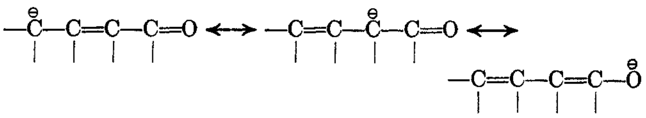
The Principle of Least Motion and the Protonation of Resonance-Stabilized Anions.—Although the principle of least motion favors the formation of the less stable isomer from the cyclohexadienyl anion, there are cases in which the formation of the most stable isomer is favored. Assigning equal weight to each of the five contributing structures for the α,α-dimethylbenzyl anion leads to a hybrid structure with bond numbers as shown below. For protonation to give cumene, the sum of the squares of the changes in bond numbers is 0.58 (the bonds in a benzene ring have a bond number of 1.5); for *para* protonation to give 3-isopropylidene-1,4-cyclohexadiene, the sum is 0.88; and for *ortho* protonation to give 5-isopropylidene-1,3-cyclohexadiene, the sum is 1.28. Experimentally, Russell observed that α,α-dimethylbenzylpotassium reacts with D_2O, DOAc, and DCl most rapidly at the exocyclic carbon atom; only for the latter two acids was ring attack observed, and in each case reaction at the *para* position was faster than at the *ortho* position.[41]

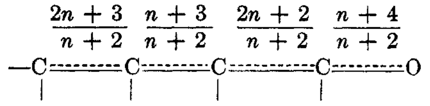


There are also cases in which the principle of least motion favors the formation of an isomer that is neither the most nor the least stable. Assignment of equal weight to each of the seven contributing structures of the cinnamyl anion leads to a hybrid structure with the following bond numbers. The sums of the squares of the changes in bond numbers are $^{129}/_{98}$, $^{45}/_{98}$, $^{150}/_{98}$, and $^{122}/_{98}$ for reaction at the α, γ, *ortho*, and *para* carbon atoms, respectively. Mixer and Young found that, under conditions where subsequent isomerization of initially formed products seemed least likely, the sodium salt of allylbenzene reacts with methanol to give more allylbenzene than propenylbenzene.[42] Although this observation seems to show that protonation occurs faster at the γ carbon atom than at the α carbon atom, it does not yield any information about protonation in the ring, since the product of such a reaction would probably not have been stable under the reaction conditions. According to the treatment developed in the previous section, however, the relative instability of such products would tend to slow their formation.



For resonance-stabilized nonhydrocarbon anions the assignment of equal weight to all important contributing structures is much more misleading than in the case of hydrocarbon anions. Unequal weighting of contributing structures could severely complicate the semiquantitative application of the principle of least motion but it need not interfere with its qualitative application. Three important contributing structures may be written for an anion that can be protonated to give either an α,β- or β,γ-unsaturated aldehyde or ketone. The greater contribution of the structure with a negative charge on oxygen can be recognized by assigning this structure a weight of n (larger than 1) relative to a weight of 1 for each of the other two structures. The hybrid anion is thereby assigned the following bond numbers. The sums of the squares of the changes in bond numbers are $(4n^2 + 4n + 1)/(n + 2)^2$ and $(2n^2 + 2)/(n + 2)^2$ for the formation of the α,β- and the β,γ-unsaturated carbonyl compounds, respectively. It is thus clear that the principle of least motion favors the formation of the unconjugated product, which has been found to be the kinetically controlled ketonic product in a number of cases.[43,44] Similar calculations show that there should be smaller changes in internal geometry in the formation of a β,γ-unsaturated nitrile than in the formation of the corresponding α,β-unsaturated nitrile by protonation of the common anion. Ingold, de Salas, and Wilson reported that the appropriate mesomeric anion yields cyclohexenylacetonitrile more rapidly than it yields cyclohexylideneacetonitrile, even though the latter product is considerably more stable.[45]





$$-\mathrm{C}\overset{\frac{2n+3}{n+2}}{=\!=\!=}\mathrm{C}\overset{\frac{n+3}{n+2}}{=\!=\!=}\mathrm{C}\overset{\frac{2n+2}{n+2}}{=\!=\!=}\mathrm{C}\overset{\frac{n+4}{n+2}}{=\!=\!=}\mathrm{O}$$

The Principle of Least Motion and Other Proton-Transfer Reactions.—From the principle of microscopic reversibility it follows that if the principle of least motion is important in carbanion protonation reactions it must also be important in carbanion formation reactions. Many of the known examples of disparity between rates and equilibria in carbanion formations[10d,11,20] may be rationalized, qualitatively at least, in terms of the principle of least motion. Thus, although nitroethane is a stronger acid than phenylacetylene by a factor that has been estimated to be 10^{11}, hydroxide ions remove protons from phenylacetylene[46] (with little probable change in the structure of the rest of the molecule) at a rate that is between 46 (assuming no isotope effect) and 460 (assuming k_H/k_T is 10) times that with which they remove protons from nitroethane[47] (with probable changes in several bond distances and bond angles as the carbon, nitrogen, and oxygen atoms move toward coplanarity).

It has recently been observed that N-methylimidazole is a less effective catalyst (by about eightfold) for the deuterium exchange of isobutyraldehyde-2-*d* than would be expected from the catalytic constants for pyridine and those of its methyl derivatives with no methyl groups adjacent to the nitrogen atom.[48] From the principle of least motion, imidazoles would

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[41] G. A. Russell, *J. Am. Chem. Soc.*, **81**, 2017 (1959).

[42] R. Y. Mixer and W. G. Young, *ibid.*, **78**, 3379 (1956).

[43] *Cf.* S. K. Malhotra and H. J. Ringold, *ibid.*, **86**, 1997 (1964), and references cited therein.

[44] Since it is felt that there are a number of other significant factors that may influence the relative rates of reaction at atoms of different elements, the present discussion is restricted largely to consideration of relative rates of reaction at different atoms of a given element.

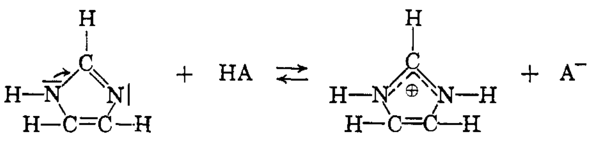
[45] C. K. Ingold, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1328 (1936).

[46] E. A. Halevi and F. A. Long, *J. Am. Chem. Soc.*, **83**, 2809 (1961).

[47] R. P. Bell and J. C. Clunie, *Proc. Roy. Soc.* (London), **A212**, 16 (1952).

[48] J. Hine, J. G. Houston, J. H. Jensen, and J. Mulders, *J. Am. Chem. Soc.*, **87**, 5050 (1965).

be expected to exhibit decreased reactivity relative to pyridines of comparable basicity, since protonation of pyridine should not greatly change its internal geometry, whereas protonation of imidazole should lengthen one carbon–nitrogen bond and shorten another so that the two become equal in length. In other words,


(5)

the electron-donating power of the single-bonded nitrogen substituent depicted by the curved arrow in eq 5 cannot operate as effectively in the transition state, where the carbon–nitrogen bond is still relatively long, as it can in the imidazolium ion, where the carbon–nitrogen bond is shorter.

Application of the Principle of Least Motion to Other Reactions.—The carbonium ions and free radicals corresponding to the mesomeric carbanions discussed in previous sections must undergo geometric changes as they react that are very similar to those undergone by the carbanions. Unfortunately, however, there appear to be fewer observations reported on such species. The α-phenylallyl (cinnamyl) cation generated by the solvolysis of α-phenylallyl chloride[49] or the ^{18}O exchange of α-phenylallyl alcohol[50] appears to react more rapidly to give α-phenylallyl than cinnamyl derivatives, under the conditions studied. In those cinnamyl halide solvolysis reactions in which the S$_N$2 mechanism is best suppressed, the yield of α-phenylallyl products tends to approach or exceed that of cinnamyl products.[51] The principle of least motion may be of importance in these reactions, in which the product stability effect would favor the formation of cinnamyl derivatives.

The cyclohexadienyl radical seems clearly to have a greater tendency to react at the center of its π-unsaturation system than at either end. Eberhardt, for example, found that the disproportionation of cyclohexadienyl radicals yields about 2.7 times as much 1,4-cyclohexadiene as 1,3-cyclohexadiene, corresponding to a 5.4-fold difference in reactivity per reactive position.[52] Similarly, James and Suart observed that the reaction of isopropyl radicals with cyclohexadienyl radicals yields more 3-isopropyl-1,4-cyclohexadiene than 5-isopropyl-1,3-cyclohexadiene in spite of the statistical factor favoring the formation of the latter compound.[53]

The reactions of 6-phenylcyclohexadienyl radicals also appear to take place preferentially to yield 1,4-cyclohexadiene derivatives,[54] although in this case the formation of 1,3-cyclohexadiene derivatives may be hindered sterically by the phenyl substituent.

Although at least one autoxidation of a "polyene," that of 1-phenyl-2-butene, appears to yield largely the nonconjugated hydroperoxide,[55] this is not the usual case.[56] Bateman has pointed out, however, that the usually observed conjugated hydroperoxide may result from rearrangement of an unconjugated peroxy radical intermediate.[56]

The products of the dimerization of the cinnamyl radical show that much of the reaction takes place at the phenylated carbon atom, but the interpretation of the reported observations is complicated by ignorance of whether the possible product 3,4-diphenyl-1,5-hexadiene is stable under the reaction conditions or not.[57]

According to the principle of least motion, reactions in which mesomeric radicals are formed should be slower than similar reactions involving the same over-all energy change in which nonmesomeric radicals are formed. The reaction of chlorine with a mixture of cyclohexane and toluene, in which the hydrogen atoms of cyclohexane are removed 2.8 times as fast as the benzyl hydrogen atoms of toluene[58] in spite of the fact that benzyl radicals are almost undoubtedly more stable than cyclohexyl radicals, is a case in which the principle of least motion may be important. When the transition state comes early in the reaction, as when a benzyl–hydrogen bond (strength 78 kcal) is broken to form a hydrogen–chlorine bond (strength 102 kcal), the C_7H_7 residue is not sufficiently coplanar for there to be much resonance stabilization. It is not implied that other factors, such as polar effects, may not also be important.

Other Explanations of Orientation in the Reactions of Mesomeric Species.—Ingold has stated, "when a proton is supplied by acids to the mesomeric anion of weakly ionizing tautomers of markedly unequal stability then the tautomer which is most quickly formed is the thermodynamically least stable."[59] This rule correctly predicts the kinetically controlled product of the protonation of many mesomeric carbanions, but it also makes incorrect predictions in several cases. A number of benzyl-type carbanions appear to be protonated more rapidly on the benzyl carbon atom than in the aromatic ring. Thus, for example, Shatenshtein has reported that when fluorene is treated with deuterioammonia, only the two hydrogen atoms of the methylene group are exchanged.[28b] Apparently, the intermediate 9-fluorenyl anion is ordinarily protonated at the 9-carbon atom. Russell has shown that α,α-dimethylbenzylpotassium reacts with various deuterated acids to afford largely 2-phenylpropane-2-*d*.[41] Another exception to Ingold's rule is found in O'Connor and Broaddus's observation that the protonation of the anion common to 1-methylsulfinyl-1-dodecene and 1-methylsulfinyl-2-dodecene yields the more stable β,γ-unsaturated sulfoxide more rapidly.[60]

Several explanations of reactions that may appear to involve mesomeric species agree in that they point out how misleading it may be to ignore surrounding species. Thus we may have ion-pair effects and leaving-group effects.[61] In reactions involving ion

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(49) G. Valkanas and E. S. Waight, *Proc. Chem. Soc.*, 8 (1959); G. Valkanas, E. S. Waight, and M. Weinstock, *J. Chem. Soc.*, 4248 (1963).

(50) C. A. Bunton, Y. Pocker, and H. Dahn, *Chem. Ind.* (London), 1516 (1958).

(51) *Cf.* J. Meisenheimer and J. Link, *Ann.*, **479**, 211 (1930).

(52) M. Eberhardt, *J. Phys. Chem.*, **67**, 2856 (1963).

(53) D. G. L. James and R. D. Suart, *J. Am. Chem. Soc.*, **86**, 5424 (1964).

(54) D. F. DeTar and R. A. J. Long, *ibid.*, **80**, 4742 (1958).

(55) J. W. Lawrence and J. R. Shelton, *Ind. Eng. Chem.*, **42**, 136 (1950).

(56) L. Bateman, *Quart. Rev.* (London), **8**, 147 (1954).

(57) H. P. Koch, *J. Chem. Soc.*, 1111 (1948).

(58) H. C. Brown and G. A. Russell, *J. Am. Chem. Soc.*, **74**, 3996 (1952); **77**, 4578 (1955).

(59) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 565, 566.

(60) D. E. O'Connor and C. D. Broaddus, *J. Am. Chem. Soc.*, **86**, 2267 (1964).

(61) *Cf.* D. J. Cram and R. T. Uyeda, *ibid.*, **84**, 4358 (1962).

pairs the position of reaction of a mesomeric species may depend on the location or nature of the gegenion. When the base B^- removes a proton from the acid HA, the acid HB formed thereby may have an advantage over any other acid in the process of reprotonation of A^-. In other reactions for which a mesomeric intermediate may be written the mechanism may actually be a concerted one not involving such an intermediate, even though earlier claims for the discovery of specific examples of such a concerted mechanism[62] have recently been controverted.[63]

Electrostatic explanations for the observed orientation in reactions of mesomeric ions have been proposed in several forms. Hammond has suggested that when the transition state in carbanion protonation comes very early in the reaction the proton may be deposited most readily near the geometric center of charge, and that when the transition state is not quite so early reaction may occur preferentially at the atom bearing the largest charge.[64] The reaction of α,α-dimethylbenzylpotassium with acids occurs preferentially at the exocyclic carbon atom, which is presumably the most negative carbon atom, but when the transition state is caused to come earlier in the reaction (by increasing the strength of the acid) protonation is seen to occur more rapidly at the *para* carbon than at the *ortho* carbons, which must be much nearer the center of charge.[41] Russell explained this observation in terms of overlapping spheres of influence of the charges on the individual atoms, but such an explanation would seem to predict lowered reactivity of the middle of the three negative atoms in the carbanions derived from β,γ- (or α,β-) unsaturated nitriles and carbonyl compounds, which is not observed.

Several workers[39,64,65a,66] have pointed out the correlation between charge densities of the various atoms and the site of reaction of mesomeric ions. It is not always obvious, however, which atom bears the largest charge. The simple resonance treatment, which leads to the prediction of bond lengths upon which a semiquantitative application of the principle of least motion can be based, often assigns the same charge to each of several atoms in a mesomeric ion, as does the simple LCAO–MO treatment. Certain more sophisticated treatments, however, do yield relative charge densities that correspond qualitatively, at least, to relative reactivities of various atoms of mesomeric ions.

To discuss the point of reaction of a mesomeric ion *solely* in terms of the charge density at various atoms of the reactant is to ignore transition-state theory. Furthermore, simple coulombic forces, which might be used in a transition-state treatment of the correlation of reactivity with charge density, do not explain the observed tendency of cyclohexadienyl radicals to react faster in the middle than at the ends of their π systems. The relative reactivities of the two types of carbon atoms in a cyclohexadienyl radical are not correlated with the free valence index, which may be calculated from bond orders[65b] to be 0.944 for the end carbons and 0.578 for the middle carbon atom. There is a correlation with the spin density, however.[53,67]

Bell attributed the change in the shape of the curves of the type shown in Figure 1 to an electrostatic effect.[11] There will be a considerable charge shift in a carbanion formation reaction, for example, as the negative charge, which early in the reaction resides largely near the positively charged proton being removed, becomes spread out more evenly over the π system as the proton is further removed. Such an effect should be of considerable importance in many cases, but, to the extent to which the negative charge in the cyclohexadienyl anion is equally distributed over the three negatively charged atoms, such an effect would be expected to be of about the same magnitude for the reaction of base with 1,4-cyclohexadiene as for reaction with 1,3-cyclohexadiene (and hence of about the same magnitude for the protonation of the mesomeric anion in each of the two possible ways), since the three negatively charged carbon atoms should be arranged roughly in the form of an equilateral triangle.

It would be interesting to learn how orientation in reactions of mesomeric carbanions with cationic acids compares with orientation in reactions with uncharged acids of the same strength. This could be determined by application of the principle of microscopic reversibility to a study of the formation of mesomeric carbanions by the action of uncharged and uninegative bases.

The fact that substituent-group electron donation and electron withdrawal by different mechanisms (p–p resonance, induction, d–p resonance, etc.) may not change in the same way as the reaction progresses may also be a factor of importance. Thus, for example, in the solvolysis of 2-chloro-2-methyl-3-butene the carbon atom on which a growing positive charge is being placed bears three substituents, two methyl groups and a vinyl group, which stabilize the incipient carbonium ion by donating electrons to the positively charged carbon atom, *i.e.*, by taking part of the positive charge upon themselves and thus diffusing the charge. There is probably a considerably larger inductive component in the electron-donating effect of the methyl substituent than there is in that of the vinyl substituent, whose effect should be almost entirely due to resonance. At the transition state the vinyl substituent should not have taken upon itself as much positive charge as it will have in the carbonium ion. There are two reasons for this: first, the carbon atom to which the vinyl group is attached has not acquired as large a positive charge in the transition state as in the carbonium ion so that it does not attract electrons as strongly from the vinyl group; second, the carbon skeleton has not yet acquired a coplanar structure in the transition state so that the vinyl substituent does not interact as efficiently with the carbon to which it is attached. The extent of inductive donation of electrons by the methyl substituents should be less in the transition state than in the carbonium ion because of the smaller charge present in the transition state, but it is probable that the noncoplanar structure interferes with the inductive effect less than it does with the

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(62) C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 1493 (1933); 93 (1934); S. K. Hsü, C. K. Ingold, and C. L. Wilson, *ibid.*, 1778 (1935).

(63) D. J. Cram and R. D. Guthrie, *J. Am. Chem. Soc.*, **87**, 397 (1965).

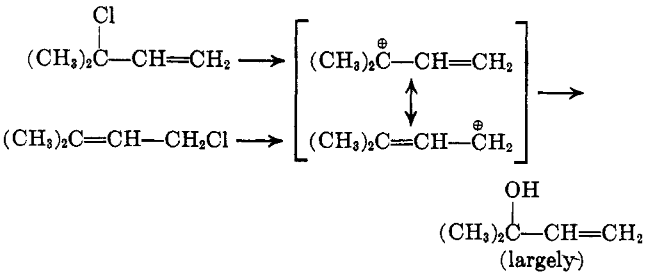
(64) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(65) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961: (a) pp 379, 418; (b) p 56.

(66) See N. Kornblum, *et al.* [*J. Am. Chem. Soc.*, **77**, 6269 (1955); **81**, 2705 (1959); **82**, 1257 (1960); **83**, 2779, 3668 (1961); **85**, 1141, 1148 (1963)], for a discussion of certain cases in which the different possible points of reaction are atoms of different elements.

(67) *Cf.* H. Fischer, *J. Chem. Phys.*, **37**, 1094 (1962).

resonance effect. If this is the case then the electron-donating power of the methyl groups relative to that of the vinyl group will be greater in the transition state than in the carbonium ion. By the principle of microscopic reversibility this will also be true in the reverse reaction, the combination of the carbonium ion with a nucleophile. It would therefore be expected that the methyl groups will stabilize the transition state involving reaction of the carbonium ion at the tertiary carbon atom, where they are attached directly to the positively charged carbon atom, more than the transition state involving reaction at the primary carbon atom, where the methyl groups can supply electrons to the reaction center only by a sterically inhibited resonance interaction through a carbon–carbon double bond. This argument thus provides an explanation for the fact that, under conditions where the SN2 mechanism is discouraged, both 1,1-dimethylallyl and 3,3-dimethylallyl halides hydrolyze to give considerably more 1,1-dimethylallyl alcohol than 3,3-dimethylallyl alcohol,[68] in spite of the fact that the latter alcohol is almost undoubtedly the more stable of the two.[69] An electrostatic argument could be given to explain the reaction of the mesomeric carbonium ion at either the primary or tertiary carbon atom. The electron-donating methyl groups will tend to take positive charge upon themselves in the carbonium ion. This positive charge at one end of the allylic system will tend to attract the π electrons so as to make the adjacent (tertiary) carbon atom less positive than the more distant primary carbon atom. This tendency to reduce like charges on adjacent atoms could thus give the primary carbon atom the largest positive charge and make it the principal reaction site. However, it can also be pointed out that the positive charges on the methyl groups will place the tertiary carbon atom nearer the *center* of positive charge. All in all it seems difficult to make an *a priori* prediction of the electrostatic effect of the larger charge on the primary carbon atom relative to the somewhat smaller charge on the tertiary carbon atom, augmented by additional charges on two of the groups attached to it.



$$(CH_3)_2C(Cl)\text{—}CH{=}CH_2 \longrightarrow \left[\begin{array}{c}(CH_3)_2\overset{\oplus}{C}\text{—}CH{=}CH_2\\ \updownarrow \\ (CH_3)_2C{=}CH\text{—}\overset{\oplus}{C}H_2\end{array}\right] \longrightarrow (CH_3)_2C(OH)\text{—}CH{=}CH_2$$

$$(CH_3)_2C{=}CH\text{—}CH_2Cl \longrightarrow$$

(largely)

Conclusion.—None of the explanations for orientation in reactions of mesomeric ions and radicals seems capable of explaining all the existing data. Unfortunately, very few experiments designed to assess the relative importance of the various possible explanations seem to have been carried out. Nevertheless, the author believes that the principle of least motion, which follows automatically from an accepted method of applying transition-state theory to the effect of structure on reactivity, may often be a factor of major importance in such reactions.

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[68] R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

[69] P. B. D. de la Mare, "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 37.

Conjugation Effects on the Low-Intensity Electronic Transition of Small-Ring Carbonyl Compounds[1,2]

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Ultraviolet absorption studies of the low-intensity n–π^* transition of *cis* and *trans* pairs of arylaroylethylenimines have been investigated. The isomer which has its carbonyl absorption maximum at longer wavelength and with a greater intensity in the ultraviolet range is the one to which the *trans* configuration has been assigned. The difference in light absorptions for the two geometrical isomers in this series are reasonably large. The results of spectral studies with the related ethylene oxide and cyclopropyl ketones were compared. Evidence is presented which demonstrates that the importance of three-ring carbonyl hyperconjugation in the n–π^* transition is a function of the heteroatom present in the small-membered ring. The conjugative effects of the three-membered ring is discussed in terms of enhanced contributions of second-order resonance structures to the hybrid in the excited state.

The electronic spectra of molecules containing three-membered rings adjacent to a carbonyl group have provided an effective method of demonstrating the conjugative properties arising from the unsaturation character of these rings.[5,6] The nature of the electrical interaction between the small ring and the carbonyl group has been described as a type of hyperconjugation which results from orbital overlap of the bent bonds of the small ring with the π orbitals of the attached carbonyl group.[7] The three-membered ring is known to possess a somewhat delocalized electronic system.[8] These delocalized electrons lie in the plane of the ring and have been attributed to the overlap

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[1] Supported in part by a research grant (NSF-GP-3972) of the National Science Foundation.

[2] Photochemical Transformations of Small-Ring Carbonyl Compounds, part IX. For part VIII. see A. Padwa and R. Hartman, *J. Am. Chem. Soc.*, **88**, 1518 (1966).

[3] National Institutes of Health Predoctoral Fellow, 1964–.

[4] National Science Foundation Undergraduate Research Participant, 1964–.

[5] R. A. Raphael, "Chemistry of Carbon Compounds," Vol. IIA, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1953, pp 25–28.

[6] L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice Hall, Inc., Engelwood Cliffs, N. J., 1963, pp 320–326.

[7] N. H. Cromwell, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **19**, 214 (1958).

[8] For a summary of leading references see A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).