

the basis for this relationship between dihedral angles and rates of elimination reactions is discussed in terms of the principle of least motion.^{26,27}

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

(27) J. Hine, *J. Org. Chem.*, **31**, 1326 (1966).

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Application of the Principle of Least Motion to the Stereochemistry of Elimination Reactions¹

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Abstract: For the transformation of ethyl chloride to ethylene, calculations are made to determine the distances the two carbon and four hydrogen atoms must move during the reaction. The geometry of the ethylene formed (relative to that of the reactant) that minimizes the sums of the squares of the distances these six atoms must move is calculated for elimination reactions with dihedral angles between the eliminated C-H and C-Cl bonds of 0° (pure *cis* elimination), 60°, 120°, and 180° (pure *trans* elimination). The calculated least-squares distances are 0.421, 1.326, 1.130, and 0.185 Å², respectively. Thus, according to the principle of least motion, there should be a tendency for pure *trans* eliminations to be faster than pure *cis* eliminations, which should in turn be faster than eliminations in which the dihedral angle is near the range 60–120°.

In the accompanying paper, the possibility was considered that the dehydrochlorination of β -benzene hexachloride involves a concerted *cis* elimination from a boat conformer.³ DePuy, Thurn, and Morris have described evidence that when the dihedral angle is near 0° such eliminations proceed more rapidly than when the dihedral angle is nearer 90°, although not as rapidly as pure *trans* eliminations, where the dihedral angle is 180°.⁴ In the present paper it will be shown that according to the principle of least motion^{1b,5} there should be a tendency for elimination reactions to be fastest when the dihedral angle is near 180°, slower when it is near 0°, and still slower when it is near the range 60–120°.

According to the principle of least motion, those elementary reactions will be favored that involve the least change in atomic position and electronic configuration.^{1b,5} In the present discussion, as in the previous application of the principle to the reactions of resonance-stabilized species, only the magnitude of changes in atomic position will be considered. It will be assumed that all the changes in atomic position take place simultaneously, and when any atomic position has undergone a certain fraction of the over-all change that it will undergo in the reaction, all the other atomic

positions have also undergone the same fraction of their final over-all change.

It is postulated that the reaction will occur in such a fashion as to involve the least expenditure of energy in changing the relative positions of atoms. The energy required to stretch or bend a bond is proportional, to the degree to which Hooke's law is applicable, to the square of the distance that the bond is bent or stretched. Therefore we shall assume that the reaction takes place so as to minimize the sums of the squares of the atomic displacements. This approach would demand that all the force constants for the displacements of various atoms be identical if it were to be completely applicable. In the present case, however, where we shall consider only the displacements, in various directions, of the various atoms in a given molecule, it amounts largely to the approximation that the various atoms move in isotropic force fields.

Calculations

For simplicity all calculations will be made for the case of the E2 transformation of ethyl chloride to ethylene. In ethyl chloride the carbon atoms are assumed to have 109° 28' bond angles and the carbon-carbon and carbon-hydrogen bond distances have been set equal to the averages of the values (1.538 and 1.104 Å, respectively) quoted by Stoicheff for such distances in saturated compounds.⁶ For ethylene, the carbon-carbon bond length, 1.337 Å, the carbon-hydrogen bond length, 1.086 Å, and the H-C-H bond angle, 117° 22', given by Allen and Plyler have been used.⁷

(6) B. P. Stoicheff, *Tetrahedron*, **17**, 135 (1962).

(7) H. C. Allen, Jr., and E. K. Plyler, *J. Am. Chem. Soc.*, **80**, 2673 (1958).

(1) (a) Part XI in the series "Polar Effects on Rates and Equilibria."
(b) For part X see J. Hine, *J. Org. Chem.*, **31**, 1326 (1966).

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(3) J. Hine, R. D. Weimar, Jr., P. B. Langford, and O. B. Ramsay, *J. Am. Chem. Soc.*, **88**, 5522 (1966).

(4) C. H. DePuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1314 (1962).

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

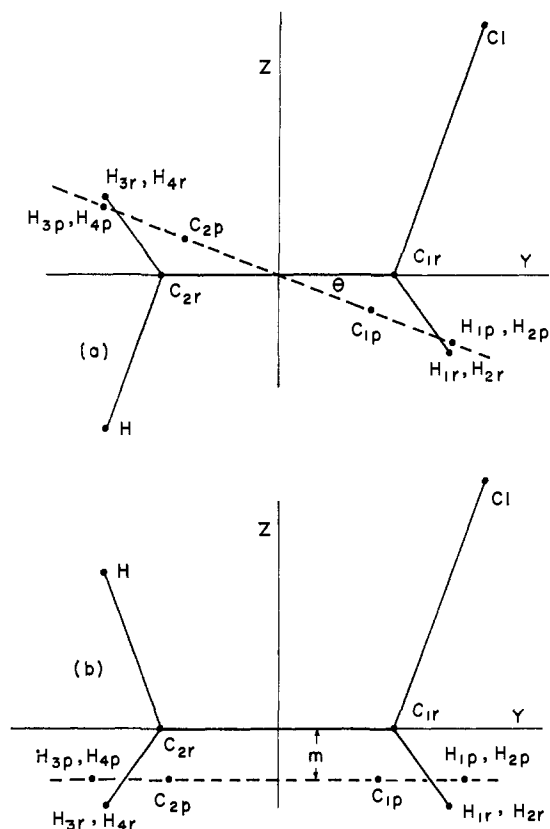


Figure 1. Models for elimination reactions with dihedral angles of (a) 180° , (b) 0° .

Let us consider first the case in which the dihedral angle between the reacting carbon-hydrogen and carbon-chlorine bonds is 180° . The immediate reactant will be a staggered conformer of ethyl chloride. A three-dimensional coordinate system is defined so that its origin is at the midpoint of the carbon-carbon bond, both carbon atoms are on the Y axis, and the chlorine atom is in the first quadrant of the YZ plane. This model is shown in Figure 1a, where H and Cl are the hydrogen and chlorine atoms removed in the reaction and C_{1r} , C_{2r} , H_{1r} , H_{2r} , H_{3r} , and H_{4r} are the carbon and hydrogen atoms of the reactant that become a part of the olefin product. In the figure, which is viewed from a direction perpendicular to the YZ plane, H_{2r} is behind H_{1r} and H_{4r} behind H_{3r} . In the reaction product, ethylene, both carbon atoms and all the hydrogen atoms except the one that is removed become coplanar. It is obvious that the sum of squares of the atomic displacements required will be a minimum if the two carbon atoms remain in the YZ plane and the plane of the ethylene molecule is perpendicular to the YZ plane and intersects it somewhere near the dashed line. The location of the various atoms in the product are denoted by the symbols C_{1p} , C_{2p} , H_{1p} , H_{2p} , H_{3p} , and H_{4p} . The only dimension remaining for a complete description of the ethylene plane and the coordinates of the atoms in the ethylene is the magnitude of the angle θ between the Y axis and the intersection of the ethylene plane with YZ plane.⁸ The coordinates of H_{1r} are denoted

(8) In this calculation no attention is given to the necessity of conservation of angular momentum. A complete treatment would be very complicated and not commensurate with the approximate character of the present treatment. Here we shall merely point out that the ethylene molecule can be given any coordinates and over-all angular momentum conserved by giving appropriate momenta to the departing hydrogen and chlorine.

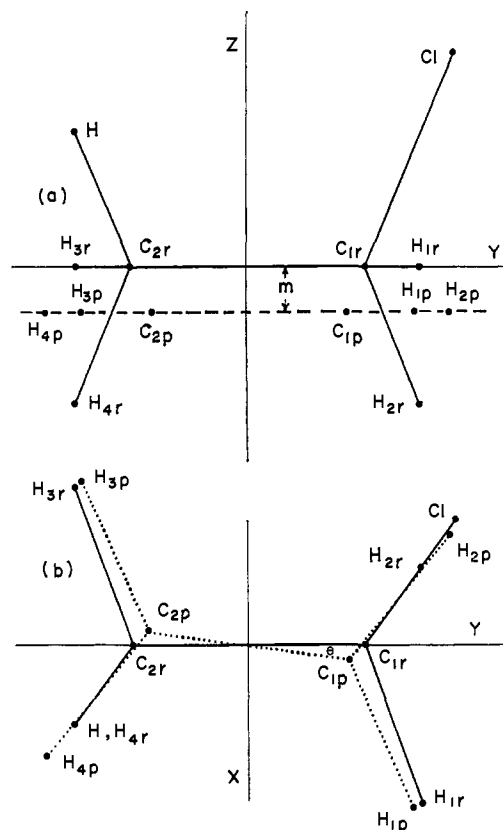


Figure 2. Model for an elimination reaction with a dihedral angle of 60° , viewed from the (a) positive X axis, (b) positive Z axis.

(x_{1r}, y_{1r}, z_{1r}) and are $(0.901, 1.137, -0.520)$, and those of C_{1r} are denoted $(x_{1r}', y_{1r}', z_{1r}')$ and are $(0, 0.769, 0)$. Those of H_{1p} —denoted (x_{1p}, y_{1p}, z_{1p}) —are $(0.928, 1.233 \cos \theta, 0.668 \cos \theta)$, and $(x_{1p}', y_{1p}', z_{1p}')$, referring to C_{1p} , is $(0, 0.668 \cos \theta, -0.668 \sin \theta)$. The distances that H_1 and C_1 move during the reaction are

$$D_{H_1} = \sqrt{(x_{1p} - x_{1r})^2 + (y_{1p} - y_{1r})^2 + (z_{1p} - z_{1r})^2} \quad (1)$$

$$D_{C_1} = \sqrt{(x_{1p}' - x_{1r}')^2 + (y_{1p}' - y_{1r}')^2 + (z_{1p}' - z_{1r}')^2} \quad (2)$$

From symmetry arguments it follows that $D_{H_1} = D_{H_2} = D_{H_3} = D_{H_4}$ and $D_{C_1} = D_{C_2}$. Therefore the sum of the squares of the distances the various atoms move is

$$\Sigma D^2 = 4D_{H_1}^2 + 2D_{C_1}^2 \quad (3)$$

This sum will be a minimum if

$$\frac{d\Sigma D^2}{d\theta} = 0 \quad (4)$$

Substitution of the appropriate values into eq 1–4 lead to the results $\theta = 21^\circ 9'$; $\Sigma D^2_{\theta=21^\circ 9'} = 0.185 \text{ \AA}^2$.

An elimination reaction with a dihedral angle of 0° , i.e., a purely *cis* elimination, must proceed *via* an eclipsed conformer, like that shown in Figure 1b, which is obtained from Figure 1a by rotating the methyl group 180° around the carbon-carbon bond. In this case the ethylene formed will lie in the plane $z = -m$, whose intersection with the XZ plane is shown by a dashed line. The coordinates of H_{1r} and C_{1r} are the same as in Figure 1a and those of H_{1p} and C_{1p} are $(0.928, 1.233, -m)$ and $(0, 0.668, -m)$, respectively. Equations

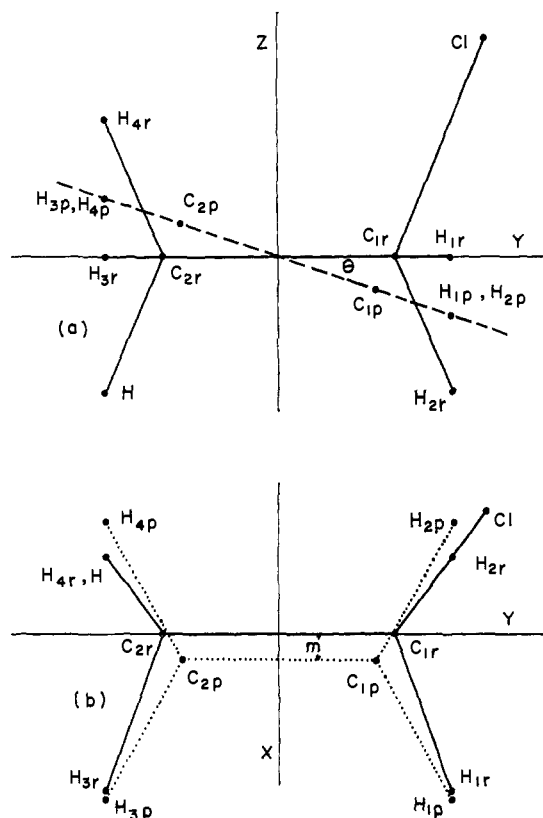


Figure 3. Model for an elimination reaction with a dihedral angle of 120° , viewed from the (a) positive X axis, (b) positive Z axis.

1-3 are still applicable, and eq 4 is replaced by

$$\frac{d\Sigma D^2}{dm} = 0 \quad (5)$$

leading to the results $m = 0.347$; $\Sigma D^2_{m=0.347} = 0.421 \text{ \AA}^2$.

For an elimination reaction with a dihedral angle of 60° , values of two parameters must be calculated to determine the least-squares location of the ethylene produced. The reacting molecule, a staggered conformer, is viewed from the positive X axis in Figure 2a and from the positive Z axis in Figure 2b. The ethylene produced will be in the plane $z = -m$, whose intersection with the YZ plane is shown by a dashed line in Figure 2a, but the C_{1p} - C_{2p} bond will not be in the YZ plane. It will pass through the Z axis making an angle θ with the YZ plane. The coordinates of C_{1r} are the same as in the two previous cases, and those of H_{1r} and H_{2r} are $(1.041, 1.137, 0)$ and $(-0.520, 1.137, -0.901)$. The coordinates of H_{1p} , H_{2p} , and C_{1p} depend on m and θ and are $(1.233 \sin \theta + 0.928 \cos \theta, 1.233 \cos \theta - 0.928 \sin \theta, -m)$, $(1.233 \sin \theta - 0.928 \cos \theta, 1.233 \cos \theta + 0.928 \sin \theta, -m)$, and $(0.668 \sin \theta, 0.668 \cos \theta, -m)$, respectively. Because of the decreased symmetry, the sums of the squares of the displacements of the atoms must be expressed

$$\Sigma D^2 = 2D^2_{H_1} + 2D^2_{H_2} + 2D^2_{C_1} \quad (6)$$

Substitution of equations of the form of (1) and (2) into eq 6, followed by the simultaneous application of eq 4 and 5, yields $m = 0.300 \text{ \AA}$; $\theta = 7^\circ 40'$; $\Sigma D^2_{m=0.300, \theta=7^\circ 40'} = 1.326 \text{ \AA}^2$.

An elimination with a 120° dihedral angle must start from an eclipsed molecule, as viewed from the

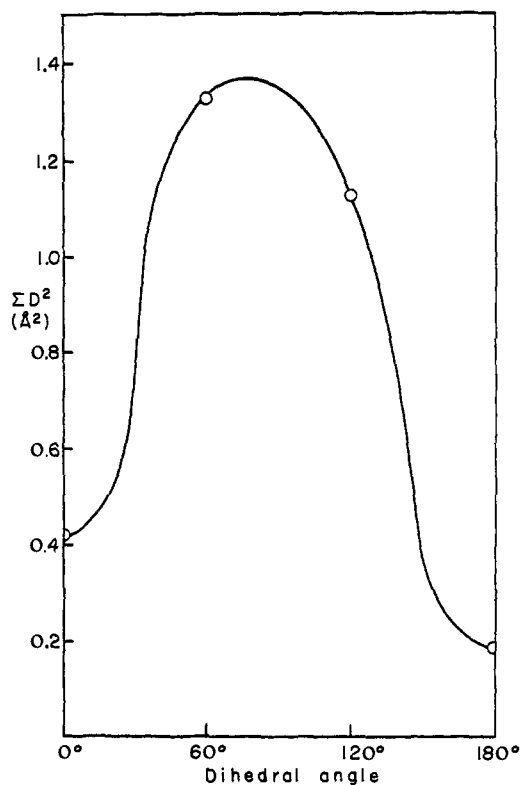


Figure 4. Plot of the sums of the squares of the distances that the atoms must move in an elimination reaction vs. the dihedral angle.

positive X axis in Figure 3a and from the positive Z axis in Figure 3b. The ethylene produced will lie in a plane perpendicular to the YZ plane and intersecting with the YZ plane as shown by a dashed line in Figure 3a. This line of intersection makes an angle θ with the Y axis. In addition the C_{1p} - C_{2p} bond is displaced from the YZ plane by the distance m in the x direction. The coordinates of H_{1r} , H_{2r} , and C_{1r} are the same as in the 60° elimination model (Figure 2). Those of H_{1p} , H_{2p} , and C_{1p} are $(m + 0.928, 1.233 \cos \theta, -1.233 \sin \theta)$, $(m - 0.928, 1.233 \cos \theta, -1.233 \sin \theta)$, and $(m, 0.668 \cos \theta, 0.668 \sin \theta)$. Application of eq 4, 5, and 6 yields $m = 0.173 \text{ \AA}$; $\theta = 18^\circ 31'$; $\Sigma D^2_{m=0.173, \theta=18^\circ 31'} = 1.130 \text{ \AA}^2$.

Discussion

A plot of the minimum sums of squares of atomic displacements vs. dihedral angle is shown in Figure 4. From the four calculated values it is clear that there are minima near 0 and 180° . Examination of models supports the intuitive conclusion that these minima are at exactly 0 and 180° . Hence, according to the principle of least motion there should be a tendency for concerted elimination reactions to proceed most rapidly when the dihedral angle is near 180° (pure *trans* elimination). Pure *cis* elimination (a dihedral angle of 0°) should be slower than pure *trans* elimination but faster than intermediate cases in which the dihedral angle differs greatly from either 0 or 180° .

In the preceding article in this series, differences in the squares of the over-all atomic displacements on the order of 0.02 \AA^2 were found to be capable of explaining activation energy differences on the order of 1 kcal/mole .^{1b} Therefore the much larger differences in squares of atomic displacements with which we are

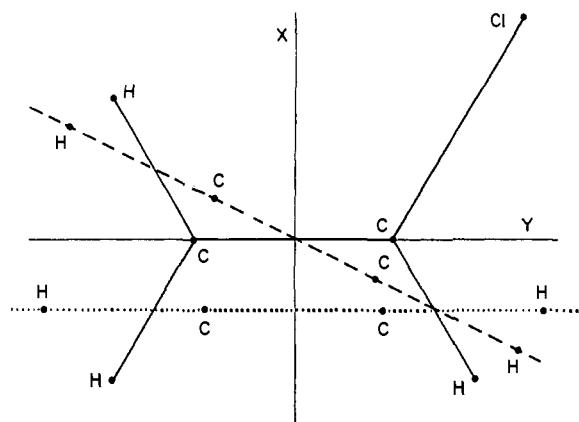


Figure 5. Acetylene formed by the *trans* dehydrochlorination (on the dashed line) and by *cis* dehydrochlorination (on the dotted line) of vinyl chloride.

dealing in the present case may be responsible for very large rate effects. The effects will no doubt be so large that, in many cases where the dihedral angle is unfavorable in the most stable conformer, elimination will occur *via* some less stable conformer or the reaction mechanism may change.

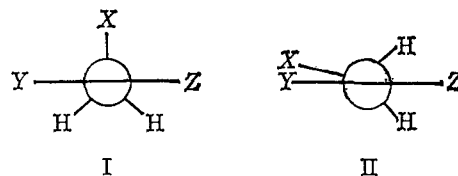
The principle of least motion seems to provide a simple and plausible explanation for the stereochemistry of elimination reactions. It is not implied, however, that other factors, such as coulombic interactions between attacking reagent and departing group,^{9,10} may not also be important.

The assumption that the two carbon atoms and the four atoms attached directly to them in the incipient olefin are moving synchronously from the positions shown in Figures 1-3 to a coplanar configuration means that the treatment that has been given will not be applicable to elimination reactions that proceed *via* intermediate carbonium ions or intermediate carbanions

(9) W. Hückel, W. Tappe, and G. Legutke, *Ann.*, **543**, 191 (1940).

(10) Cf. S. J. Cristol, N. L. Hause, and J. S. Meek, *J. Am. Chem. Soc.*, **73**, 674 (1951).

in which the negatively charged carbon atom has a planar configuration. In a case of the latter type, the sum of the squares of the distances the remaining atoms must move to achieve coplanarity will be a minimum when the departing anion is located like *X* is in I and a maximum when it is located near where *X* is in II.



An analogous statement could be made for eliminations *via* carbonium ions. For eliminations *via* pyramidal carbanions the treatment given for concerted eliminations is applicable when appropriate consideration is given to the possibility of inversions in the configuration of the carbanion.

The principle is also applicable to the formation of triple bonds. The straight line that could be reached by the acetylene being formed by a *trans* dehydrochlorination of vinyl chloride with the least-squares motion of the constituent atoms is shown in Figure 5 by a dashed line. The corresponding line for a *cis* elimination is shown by a dotted line. It is clear that the minimized sum of the squares of the distances the atoms must move in the reaction is considerably less for the *trans* elimination. This provides an explanation for the greater facility of *trans* eliminations in the formation of acetylenes, both in the cases of concerted elimination and in the cases where nonlinear carbanions are intermediates.¹¹⁻¹³

Acknowledgment. Support of this investigation by the National Science Foundation, under Grants GP-2002 and GP-4445, is gratefully acknowledged.

(11) S. I. Miller and R. M. Noyes, *ibid.*, **74**, 629 (1952).

(12) S. J. Cristol, A. Begoon, W. P. Norris, and P. S. Ramey, *ibid.*, **76**, 4558 (1954), and references cited therein.

(13) S. I. Miller, *J. Org. Chem.*, **26**, 2619 (1961).