(1946).

2. H. Gilbert, F.F. Miller, S.J. Averill, E.J. Carlson, U.L. Folt, H.J. Heller, F.J. Stewart, R.F. Schmidt, and H.L. Trumbull, *J. Am. Chem. Soc.*, **78**, 1669 (1956).

3. J.B. Kinsinger, *Makromol. Chem.*, **35**, 132 (1959).

4. N.G. Gaylord and A. Takhashi, *"Addition and Condensation Polymerization Processes"*, (*Adv. Chem. Ser.*, **91**), R.F. Gould, Ed., American Chemical Society, Washington, D.C., 1969, p. 94.

5. M. Hirooka, *XXIII Intern. Congr. Pure Appl. Chem. Macromol. Preprints*, **1**, 311 (1971).

6. H.K. Hall, Jr. and J.W. Rhoades, *J. Polym. Sci.*, **A-1, 10**, 1953 (1972).

7. I. Cho and J.Y. Lee, *Macromolecules*, **16**, 1245 (1983).

8. I. Cho and J.Y. Lee, *J. Polym. Sci., Polym. Lett., Ed.*, **21**, 389 (1983).

9. H.K. Hall, Jr., H.A.A. Rasoul, M. Gillard, M. Abdelkader, P. Nogues, and R.C. Sentman, *Tetrahedron Lett.*, **23**, 1245 (1983).

10. C.J. Ireland, K. Jones J.S. Pizey, and S. Johnson, *Synth. Commun.*, **6**, 185 (1976).

11. H.K. Hall, Jr., K.E. Reineke, J.H. Ried, R.C. Sentman, and D. Miller, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 361 (1982).

12. J.Y. Lee and I. Cho, *J. Polym. Sci., Polym. Chem. Ed.*, submitted.

13. A.B. Padies, S.T. Hedrick, and H.K. Hall, Jr., *J. Org. Chem.*, **48**, 3787 (1983).

Location of Transition States by the Conjugate Reaction Coordinate Method

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A relatively simple method of locating the saddle point is presented. In this method a single determination of the saddle point location by constrained energy minimizations for points selected on the assumed saddle surface provides us with the structure, location and energy of the TS, the reaction path at the saddle point and characterization as the TS. Some examples were given.

Introduction

The determination of transition states (*TS*) plays a central role in visualizing and predicting mechanisms of chemical rate processes, since they represent saddle points between the two local minima on energy surfaces corresponding to reactants and products. The experimental determination of *TS* geometries, however, is extremely difficult; the theoretical determination also presents great difficulties albeit various computational methods of saddle point location have been proposed.[1-4]

In this paper we report a relatively simple method for locating the saddle point (*T*) from which the *TS* itself can be obtained. The method automatically characterizes the *TS* by determining two rectangular coordinate axes (with origin at the saddle point *T*) representing the reaction path, ξ, (reaction coordinate, *RC*) and the direction orthogonal to it, η, (orthogonal coordinate, *OC*) on the saddle surface of the hyperbolic paraboloid (eq. 1) shown in Figure 1.

$$\varepsilon\,(\xi, \eta) = A\,\xi^2 + B\,\eta^2 \qquad (1)$$

where $A < 0$ and $B > 0$

Method

The potential energy E of a molecule depends on a set of molecular coordinates $\{q_i\}_{i=1}^n$, and a constrained minimum energy surface with respect to the two, x and y, can be expressed as
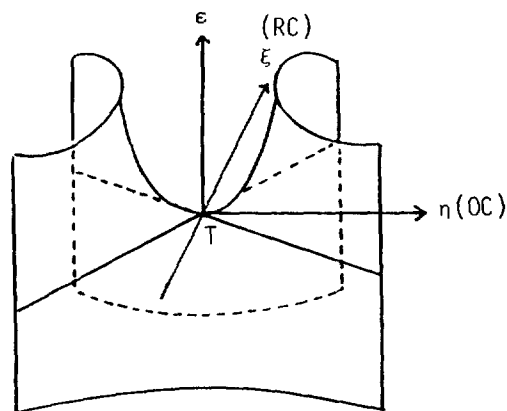

Figure 1. Hyperbolic paraboloid potential energy surface, $\varepsilon = A\xi^2 + B\eta^2$, where $A < 0$ and $B > 0$, showing the reaction coordinate(ξ) and the orthogonal coordinate(η) with the origin at the saddle point(T).

$$E\,(x, y) = \min.\ \{E\,(q_1, q_2, \cdots\cdots q_{n-2}, x, y)\} \qquad (2)$$

The energy E(x,y) defines a minimum energy surface in the sense that the molecular system is constrained to achieve an energy minimum regarding the remaining n-2 coordinates.

A saddle point on this surface should satisfy the following conditions.[5]

$$(\mathrm{i})\ \ \frac{\partial E}{\partial q_i} = 0\ \ \text{for all coordinate } i, \qquad (3a)$$

(ii) $\dfrac{\partial^2 E}{\partial q_r^2} < 0$ for only one coordinate q_r,   (3b)

(iii) $\dfrac{\partial^2 E}{\partial q_j^2} > 0$ for all other coordinates q_j $(j \neq r)$ (3c)

Assuming that the energy surface is quadratic in the close region of the (nondegenerate) saddle point, we have in general,

$$E(x, y) = ax^2 + by^2 + 2cxy + 2dx + 2ey + f \tag{4}$$

where a,b,c,d,e and f are constants. Application of condition (i) for $q_i = x$ and y leads to the location $(x^\ast, y^\ast)$ and energy $E^\ast$ of the saddle point (T) in terms of the constants a-f.

$$x^\ast = \frac{bd - ce}{c^2 - ab}, \quad y^\ast = \frac{ae - cd}{c^2 - ab} \tag{5}$$

$$E^\ast = f - (ax^{\ast 2} + by^{\ast 2} + 2cx^\ast y^\ast) \tag{6}$$

If our assumption of a quadratic potential surface holds for the close region of the saddle point, we may transform eq (4) to a simple form of the hyperbolic paraboloid, eq (1), by rotation and translation of the coordinate frame (x,y). Thus rotation (Figure 2) defines a new rotated coordinate frame (X,Y) which in turn is transformed into the final coordinate frame (ξ,η) by translation of the origin on to the saddle point $(x^\ast,y^\ast)$.

$$(x, y) \xrightarrow{\text{rotation}} (X, Y) \xrightarrow{\text{translation}} (\xi, \eta)$$

Interrelationships between the coordinate systems can be given by equations (7) and (8).

$$\begin{aligned} X &= x \cos \alpha - y \sin \alpha \\ Y &= x \sin \alpha + y \cos \alpha \end{aligned} \tag{7}$$

where angle α is defined relative to the rotated axis X as shown in Figure 2.

$$\begin{aligned} \xi &= x' \cos \alpha - y' \sin \alpha \\ \eta &= x' \sin \alpha + y' \cos \alpha \end{aligned} \tag{8}$$

where $x' = x - x^\ast$ and $y' = y - y^\ast$.

Algebraic manipulations involving equations (4) and (8) lead to eq. (1), which should satisfy the condition (ii) and (iii) above.
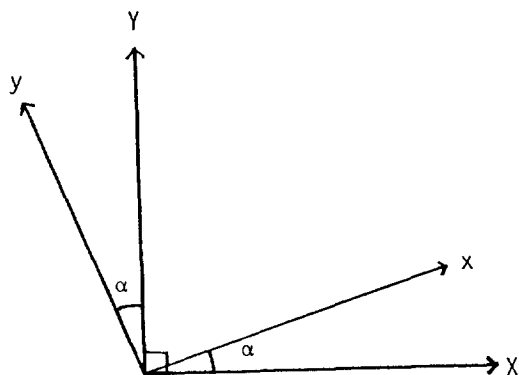

Figure 2. Rotation of coordinate frame from (x,y) to(X,Y).

$$\varepsilon(\xi, \eta) = A \xi^2 + B \eta^2 \tag{1}$$

where $\varepsilon(\xi, \eta) = E - E^\ast$

$$A = \frac{a \cos^2\alpha - b \sin^2\alpha}{\cos 2\alpha} < 0$$

$$B = \frac{-a \sin^2\alpha - b \cos^2\alpha}{\cos 2\alpha} > 0 \tag{9}$$

The angle α can be given in terms of the constants a, b and c.

$$\alpha = \frac{1}{2} \tan^{-1}\left(\frac{2c}{a - b}\right) \tag{10}$$

Determination of the constants a-f will therefore enables one to obtain the location (eq. 5) and energy (eq. 6) of the saddle point with the reaction path (ξ) relative to the original coordinate axis x (eq. 10). Geometry optimization at the saddle point $(x^\ast, y^\ast)$ will give us the transition state structure.

Procedure

(i) First of all select two variables x and y among all those which are needed to describe the potential energy surface. The two chosen should be those which are considered to be most significant in connection with the given reaction; they are normally a pair which varies in a conjugate manner (hence is called a conjugate reaction coordinate, CRC, method), e.g., a pair of bonds that is forming and breaking concertedly as in S_N2 reactions and in Cope and Claisen rearrangements etc, a pair of bonds that is either forming or breaking concertedly but not in a synchronous manner as in the hetero–Diels–Alder reactions[6] and in other dipolar intermolecular cycloaddition reactions etc., and a pair of angles of rotation in a conformational change of a molecule etc.

(ii) Make an initial guess at the saddle point T and obtain an approximate square grid region of the potential energy (quadratic) surface around it, then select a set of points {x,y} within this region. The number of points should be greater than six since there are 6 unknowns (a-f) to be determined in a simultaneous solution of the constants in eq. (4).

(iii) The potential energy E is evaluated by the energy minimization with respect to the rest of the n–2 coordinates over the grid of selected points (x,y) which span the saddle point. The position of the saddle point is found by inspection of the calculated values of E. Then use only those points falling on the two columns corresponding to the assumed RC and OC on the saddle surface (Figure 3) in determination of the best values of the constants a-f by either solving a simultaneous equations consisting of more than six equations (4) with the known x, y, and E, or by either multiple linear regression.[7]

(iv) Using the constants a-f, obtain $x^\ast$, $y^\ast$, $E^\ast$ and α. Confirm that the point corresponding to $(x^\ast, y^\ast)$ is a true TS by checking A<0 and B>0 using eq. 9.

(v) Refinement can be achieved by minimizing the gradient norm.

Results and Discussion

It is obvious that the success with this method depends on the good initial guess of the saddle point and the number of

points (the greater, the better) used in the calculation of the constants a–f. Since we are assuming a quadratic surface (eq. 4), the points lying outside of the quadratic region will not help improving the constants.

The most important merit of this method is its simplicity, besides the following attractive features: (a) this method gives the reaction path (ξ) at the saddle point by a single determina-
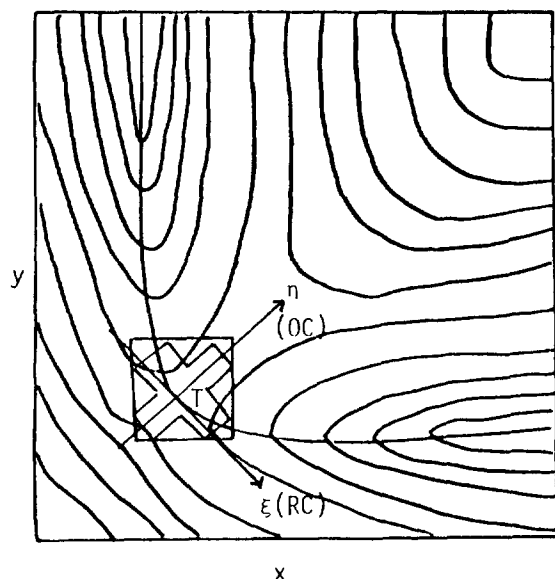

Figure 3. Typical potential energy hypersurface with two-RC's. Multiple regressions were performed in two ways; (i) with all data points within square grid, (ii) with points within columns of assumed-RC and –OC.

tion of the saddle point, (b) the signs of A and B automatically confirm that the point (x*, y*) is a true TS; in other methods extra computation is required to confirm the TS by Force Program, (c) the magnitude of the constant A and B provides information on the TS structure; a small value will indicate a relatively flat saddle point and hence a loose TS whereas a large value indicates a tight TS, (d) relatively inexpensive constrained energy minimization can be used so that substantial reduction of computer time is possible compared to other method (*vide infra*). (e) it appears that a rather simple and crude initial guess of the saddle point based on chemical intuition can yield a satisfactory starting point for this method.

Examples

To test the practical performance of the method we have carried out calculations using the MNDO energy minimization program[8] on some chemically important classes of reaction.

Cope and Claisen Rearrangements. A conjugate pair of bonds involved in these types of reaction is one that is breaking (x) and the other that is forming (y). In the model Cope rearrangement,[3] the points were selected by varying x and y in the range of x = 1.57 – 1.61 A and y = 1.78 – 1.82 Å in 0.01 Å increments. The results obtained using the procedures above are shown in Table 1. The method (ii) in which only those points falling on the two columns corresponding to the RC and OC in Figure 3 gives, as expected, a better correlation. The agreement with the results of other method,[3] is excellent. Likewise in the Claisen rearrangement,[3] the points were obtained by varying x and y in the range of x = 1.44 – 1.48 Å and y = 1.86 – 1.90 Å similarly as above, in 0.01 Å increments. Again the method (ii) is better and agreement with

Table 1. Summary of saddle point locations by the conjugate reaction coordinate method. The method (i) includes all points within the square grid while the method (ii) only those falling on the RC and OC columns in Figure 3

Reaction	Method	NDP[a]	x*[b,c]	y*[b,c]	E*[c,d]	A	B	r[e]
Cope rearrangement	(i)	25	1.5934	1.8021	61.0770	–91.07	315.17	0.947
			1.59[f]	1.80[f]	61.0[f]			
	(ii)	11	1.5936	1.7994	61.0714	–126.37	329.43	0.991
Claisen rearrangement	(i)	25	1.4553	1.8781	32.2716	–151.85	316.86	0.987
			1.46[f]	1.88[f]	32.3[f]			
	(ii)	14	1.4552	1.8779	32.2745	–185.29	341.25	0.989
CH₃F + H⁻	(i)	25	1.3345	1.5654	12.1629	–40.38	151.50	0.940
			1.26[g]	1.68[g]	11.5[g]			
	(ii)	13	1.2897	1.6531	11.6446	–67.68	187.23	0.993
CH₃F + CH₃⁻	(i)	25	1.8692	1.5889	14.6439	–65.67	118.72	0.974
			1.79[g]	1.61[g]	14.0[g]			
	(ii)	11	1.8130	1.6143	13.9775	–87.88	163.76	0.997
CH₃F + Cl⁻	(i)	25	1.9941	2.2034	–41.6603	–66.47	132.54	0.975
			1.95[g]	2.20[g]	–43.1[g]			
	(ii)	12	1.9825	2.1658	–41.6197	–82.41	149.68	0.993
CHOCOCHO rotation	(i)	28	90	186	–77.71765[h]	–2.59	2.25	0.994
			91	183[i]	–77.66640[h,j]			
	(ii)	16	90	186	–77.71763[h]	–3.16	2.20	0.994
C₄H₄O + C₂H₄[k]	(ii)	6	1.9964	2.1124	46.45	–137.91	1076.21	1.000

[a]Number of data points. [b]Bond lengths in Å, angles in degree. [c]Literature values are given in parentheses. [d]Energies in kcal/mol unless indicated otherwise. [e]Correlation coefficient obtained by multiple linear reference 3. [f]From refeence 3. [g]From reference 10. [h]In a. u. [i]From reference 10. [j]Energy with standard geometries from reference 11. [k]From reference 6.

the results of Dewar *et. al.*[3,9] is excellent.

S_N2 Reaction. The S_N2 reaction is one of the most thoroughly studied class of reaction in chemistry by experimental as well as theoretical method. Here the conjugate pair of bonds is one that is breaking, x, and the other forming, y, concertedly. We have carried out calculations on the nucleophilic displacement of fluoride in CH_3F by H^-, CH_3^-, and Cl^-.

$$CH_3F + X^- \rightarrow CH_3X + F^- \tag{11}$$

where $X = H, CH_3, Cl$
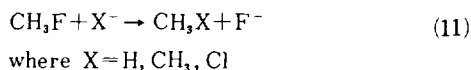
In the selection of points within the square grid that span the saddle point, the two coordinates were varied in 0.1 Å increments in the range of x = 1.06 – 1.46 Å and y = 1.37 – 2.07 Å for X = H, x = 1.59 – 1.99 Å and y = 1.41 – 2.01 Å for X = CH_3, and x = 1.76 – 2.26 Å and y = 1.87 – 2.47 Å for X = Cl. Results of our calculations in Table 1 compare well with those by other method.[10] In order to assess the efficiency of the present method, numbers of SCF cycle needed to arrive at the TS structure are compared in Table 2 with those of widely used reaction coordinate method.[1,3,4,10] Reference to this table indicates that the numbers are substantially less and hence more efficient with our method for the two cases (X = H and CH_3). For X = Cl the reaction coordinate method appears to be more efficient. but this is due to the high endothermicity of the reac-

Table 2. A comparison of the number of SCF cycles

Reaction	Present method	Reaction coordinate method
$CH_3F + H^-$	68	124[a]
$CH_3F + CH_3^-$	63	85[b]
$CH_3F + Cl^-$	73	31[c]

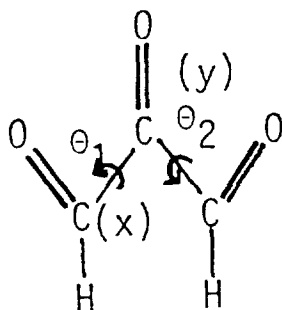[a]From product complex in 0.2 Å increments. [b]From reactant complex in 0.2 Å increments. [c]From product complex in 0.2 Å increments.

Figure 4. Conformational change of propanetrione.

tion giving very similar TS structure to the product complex which was adopted as the starting point. Moreover it is well known that for this reaction (X = Cl) the reaction coordinate method fails to give continuous reaction path leading to the TS when one starts from the reactant complex.

Rotational Surface of Propanetrione. The rotation-rotation surface of the propanetrione (Figure 4) has been studied by the X-method[11] of the saddle point location using the standard CNINDO program.[12] We have therefore undertaken an examination of this system with the CRC method. Computations were performed as a function of the two dihedral angles $\theta_1(x)$ and $\theta_2(y)$ in Figure 4, which represents the structure corresponding to $\theta_1 = \theta_2 = 0°$. The angles were varied in 10° increments in the range of x = 60-120° and y = 170-200°. The results in Table 1 show small discrepancies from these of the X-method. Since in the present method we used GEOMO/RV[13] for the constrained geometry optimization with the CNDO/2 method, the small differences in x and y values appear to have resulted from the difference in the method of computation.

References

1. K. Müller. *Angew. Chem.*, **19**, 1 (1980).
2. P. Scharfenberg, *J. Comput. Chem.*, **3**, 277 (1982).
3. M.J.S. Dewar, E.F. Healy, and J.J.P. Stewart, *J. Chem. Soc. Faraday Trans. II*, **80**, 277 (1984).
4. For a recent review see, S. Bell and J.S. Crighton, *J. Chem. Phys.*, **80**, 2464 (1984).
5. L. Salem, "Electrons in Chemical Reaction: First Principles," John-Wiley & Sons, New York, 36 (1982).
6. I. Lee, E.S. Han, and J.Y. Choi, *J. Comput. Chem.*, **5**, 606 (1984).
7. J.L. Kuesten and J.H. Mize, "Optimization Techniques with Fortran," McGraw-Hill, New York, 205 (1973).
8. M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907, 5231 (1977).
9. M.J.S. Dewar and E.F. Healy, *J. Am. Chem. Soc.*, **106**, 7127 (1984).
10. I. Lee, B-S. Lee, and C.H. Song, *Bull. Korean Chem. Soc.*, **6**, 191 (1985).
11. P.G. Mezey, M.R. Peterson, and I.G. Csizmadia, *Can. J. Chem.*, **55**, 2941 (1977).
12. QCPE Program No. 141, Indiana University, Bloomington, Indiana.
13. QCPE Program No. 350, Indiana University, Bloomington, Indiana.