solid, **20** (46%): IR 1720–1650 (ν(TaH)), 1275, 1205, 1025, 940, 900, 835, 740, 715, 695, 490 cm^{-1}. Anal. Calcd for $C_{23}H_{39}NPTa$: C, 51.02; H, 7.26; Ta, 33.42 (mol wt 542). Found: C, 50.94; H, 7.08; Ta, 33.41 ((C_6H_6, Singer method) mol wt 550).

Cp*Ta(NCMe$_3$)(OCHMe$_2$)$_2$ (21). An NMR tube sealed to a ground-glass joint was loaded with Cp*Ta(NCMe$_3$)H$_2$(PMe$_2$C$_6$H$_5$) (**17**, 75 mg, 0.038 mmol), acetone (59 torr in 25.3 mL, 0.080 mmol), and 0.3 mL of benzene-d_6, and sealed with a torch. After 3 days at 25 °C and 1 h at 80 °C, the volatiles were removed leaving **21**: IR (C_6H_6) 1275 (st, ν(TaNC)), 1215, 1120, 1030, 995, 980, 845, 740 cm^{-1}.

Cp*Ta(NCH$_2$CMe$_3$)(OCHMe$_2$)$_2$ (22). **22** was prepared from Cp*Ta(NCH$_2$CMe$_3$)H$_2$(PMe$_2$C$_6$H$_5$) (**20**, 75 mg, 0.14 mmol) and acetone (150 torr in 33 mL, 0.27 mmol) by a procedure analogous to the synthesis of **21**: IR (C_6H_6) 1280 (st, ν(TaNC)), 1120, 995, 980, 860, 840, 585 cm^{-1}.

Cp*Ta(CH$_2$NMe)Me(PMe$_3$)H (23). A thick-walled glass reaction vessel with Teflon needle valve, charged with 1.86 g of Cp*Ta(CH$_2$NMe)Me$_2$ (**3**, 4.78 mmol), 5 mL of benzene, PMe$_3$ (1100 torr in 104 mL, 6.15 mmol), and 4 atm of H$_2$, was stirred at 25 °C for 24 h. After the volatiles were removed, recrystallization from petroleum ether gave 1.01 g of red **23** (39%): IR 1680 (ν(TaH)), 1490, 1280, 1240 (st), 1025, 955 (st), 935, 900, 720, 665, 480, 450. Anal. Calcd for $C_{16}H_{33}NPTa$: C, 42.58; H, 7.37; N, 3.10 (mol wt 451). Found: C, 42.35; H, 7.15; N, 2.91 ((C_6H_6, Bernhardt) mol wt 478).

Cp*Ta(CH$_2$NMe)Me(OCHMe$_2$) (24). A solution of Cp*Ta(CH$_2$NMe)Me(PMe$_3$)H (**23**, 25 mg, 0.046 mmol) and acetone (41 torr in 25.3 mL, 0.056 mmol) in 10 mL of petroleum ether was stirred at −80 °C for 30 min and at 25 °C for 30 min. Removal of the volatiles left **24**, 70% pure (by NMR): **24** is extremely soluble in hydrocarbon solvents: IR (C_6D_6) 1270, 1160, 1130 (st), 1000 (st), 970, 905, 850, 620 cm^{-1}.

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Registry No. 1, 69302-75-6; **2**, 84876-02-8; **2-d_6**, 84876-20-0; **3**, 84894-72-4; **4**, 84876-03-9; **5**, 84894-73-5; **6**, 84876-04-0; **7**, 84894-74-6; **8**, 84876-05-1; **9**, 71763-35-4; **10**, 84849-50-3; **11**, 84876-06-2; **12**, 84876-07-3; **13**, 84876-08-4; **14**, 84876-09-5; **15**, 84876-10-8; **16**, 84876-11-9; **17**, 84876-12-0; **18**, 84876-13-1; **19**, 84876-14-2; **20**, 84876-15-3; **21**, 84876-16-4; **22**, 84876-17-5; **23**, 84876-18-6; **24**, 84876-19-7; LiNMe$_2$, 3585-33-9; LiN(Me)CH$_2$CH$_2$CH$_3$, 84876-21-1; LiN(CHMe$_2$)$_2$, 4111-54-0; LiN(H)CH$_2$CMe$_3$, 84876-22-2; LiNHMe, 37123-26-5; NaOCHMe$_2$, 683-60-3; LiOMe, 865-34-9; LiCH$_2$CMe$_3$, 3710-27-8; KCH$_2$C$_6$H$_5$, 2785-29-7; (2-methylallyl)magnesium chloride, 563-47-3.

Relationship between More O'Ferrall Plots and Marcus Rate Theory. Overriding Orbital Symmetry Constraints on Chemical Reactions

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Abstract: "More O'Ferrall" plots have seen increasing use in recent years for qualitatively interpreting substituent effects on rates of a wide variety of reactions, including nucleophilic substitution, elimination reactions, proton transfers, carbonyl additions, sigmatropic shifts, and Diels–Alder reactions. In the present paper it is shown that the main idea behind the More O'Ferrall plot (geometric distortions along the reaction coordinate ("parallel" effects) and geometric distortions along orthogonal coordinates ("perpendicular" effects)) can be used to derive a quantitative expression for the reaction barrier that is very similar to the Marcus equation, now being applied to electron and proton transfer reactions, as well as nucleophilic substitutions. It is found that the perpendicular effects of the More O'Ferrall approach enter into the intrinsic barrier term of Marcus' equation. Application of this Marcus-like equation to cycloadditions and sigmatropic shifts shows that intrinsic barriers are a function of orbital symmetry constraints and are highly dependent on substituents. This large dependence can provide a mechanism for dramatic reductions in the barriers of both symmetry-allowed and symmetry-disallowed processes.

I. Introduction

The use of More O'Ferrall plots[1] and Marcus rate theory[2] for interpreting substituent effects on reaction rates has been widespread in recent years.[3,4] Both approaches have lent considerable insight into the nature of chemical reactions, and it would be worthwhile to explore the consequences of certain assumptions behind the More O'Ferrall plot. These assumptions can be shown to lead to a quantitative equation similar in many respects to the Marcus equation.

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A. Marcus Equation. The Marcus equation is given by

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + \tfrac{1}{2}\Delta G^{\circ} + (\Delta G^{\circ})^2/16\Delta G_0^{\ddagger} \qquad (1)$$

where $\Delta G^{\ddagger}$ is the barrier of a reaction, ΔG° is the free energy difference between reactants and products, and $\Delta G_0^{\ddagger}$ is the "intrinsic" barrier. The Marcus equation has generally been applied to group transfer reactions (e.g., electron, proton, atom, methyl transfer) which can be represented as

$$\text{A–B} + \text{C} \rightleftarrows \text{A} + \text{B–C} \qquad (2)$$

$$\text{A–B} + \text{A} \rightleftarrows \text{A} + \text{B–A} \qquad (3)$$

$$\text{C–B} + \text{C} \rightleftarrows \text{C} + \text{B–C} \qquad (4)$$

The "intrinsic" barrier, $\Delta G_0^{\ddagger}$, has usually been taken to be the average barrier of the two symmetrical transfer reactions (eq 3 and 4) and has been interpreted as the nonthermodynamic, or *kinetic*, contribution to the barrier of the *unsymmetrical* reaction. The $^1/_2\Delta G^{\circ}$ term represents the *thermodynamic* contribution and raises or lowers the kinetic component of the barrier according to whether the reaction is endergonic or exergonic. The first two terms of Marcus' equation are exact when the free energy of the transition state, A–B–C, is the average of the free energies for A–B–A and C–B–C.[4j–l,5] The third term, $(\Delta G^{\circ})^2/16\Delta G_0^{\ddagger}$, represents an approximate correction for nonadditivity and depends on the relative magnitude of ΔG° and $\Delta G_0^{\ddagger}$.

The Marcus equation was originally derived to describe barriers to electron-transfer reactions by employing a weak overlap assumption which is valid to the extent that transition-state interactions between the orbitals of the reacting molecules are zero.[2] This condition appears to be appropriate to certain classes of electron-transfer reactions, and Marcus extended eq 1 to proton and atom transfers by demonstrating empirical correlations[4a] and by showing[6] that the mathematical form of eq 1 is similar to the form of the BEBO equation,[7] which is derived specifically for radical transfer processes. Somewhat later, it was shown[4c] that eq 1 could be obtained without the weak overlap approximation by applying equivalent group assumptions,[8] which provide the basis for *linear* free energy relationships such as the Brønsted[9] and Hammett equations,[10] to the *derivative* of the free energy change with respect to a perturbational parameter. More recently, it has been shown[11] that Marcus' weak overlap approximation actually holds for first-order corrections to Hartree–Fock SCF wave functions, and, from certain relationships describing the response of the electronic kinetic energy to substituent effects, it has been possible to obtain[4j,l] a general barrier equation[12] for which the Marcus equation and about a dozen other empirical equations[4j,l] are special cases. All of the equations give similar predictions for the barrier height. Even more recently, it has been shown that certain constraints (i.e., a "scaled symmetry relationship")[13] on the form of a reaction coordinate function can lead to the Marcus relationship. Eckart's function[14] exhibits the scaled symmetry relationship, and it has been known[15,16] for some time that Eckart's function obeys eq 1.[17]

Marcus' equation has seen widespread application to solution reactions,[4] but, with few exceptions, the usual approach has been to measure $\Delta G^{\ddagger}$ and ΔG° and to calculate $\Delta G_0^{\ddagger}$ by assuming that the intrinsic barrier is independent of ΔG°.[4a,b,d,e] For many reactions there is no easy alternative.[4e] For n identity reactions (eq 3 and 4) there are $n(n-1)/2$ unsymmetrical reactions (eq 2) and by measuring $\Delta G^{\ddagger}$ of the latter, Marcus' equation can be used to obtain intrinsic barriers for each identity reaction. Since there are more experimental measurements than parameters to be calculated, independent checks on the calculated $\Delta G_0^{\ddagger}$ values are possible, and Lewis,[4g] and Pellerite and Brauman[4h] have provided excellent examples for solution-phase S_N2 and gas-phase S_N2 reactions, respectively. Direct measurements of both identity barriers associated with one cross reaction have been rare: examples have been reported for proton transfer reactions between substituted fluorenyl anions and the corresponding hydrocarbons,[4k] for hydride transfer reactions[4i] and for proton-bound dimers of amines, neutral first- and second-row hydrides, and anions in the gas phase.[4j,18] Computed SCF barriers and well depths of various identity and cross reactions have also been shown to follow the Marcus relationship reasonably well.[4j,l,m,19]

The Marcus equation provides a simple picture of how thermodynamic and kinetic substituent effects combine to affect the overall barrier to a group transfer reaction. It can account for the rate–selectivity principle,[20] and thermodynamic control when substituent effects dominate the ΔG° terms in eq 1 and can account for kinetic control and the breakdown of the rate–selectivity principle when substituent effects dominate the $\Delta G_0^{\ddagger}$ terms.[4j,l] The degree of curvature observed in a Brønsted-type relationship can also be interpreted in terms of the relative magnitude of ΔG° and $\Delta G_0^{\ddagger}$.[2,12,23,24] The Marcus equation has not been extensively applied to non-group-transfer reactions since there is no analogy to the identity reactions.[21] The results which follow in section II, as well as previous work,[4c,13] provide a foundation for the application of Marcus-like relationships to addition reactions, intramolecular rearrangements and other examples of non-group-transfer reactions.

B. More O'Ferrall Plot. The Marcus equation is a relationship between the energy of a saddle point[22] on a potential energy surface and the energy of the reactants or products. Some workers[6,16] have interpreted the derivative, $d\Delta G^{\ddagger}/d\Delta G^{\circ} = \alpha$, as equivalent to the fractional displacement of the saddle-point position along the reaction coordinate, so that the Marcus equation can be interpreted to give some structural, as well as energetic, information concerning the changes in geometry and energy which occur along the reaction coordinate.[13] In this sense, the Marcus relationships can be considered[4c,13] as quantitative extensions of Hammond's postulate,[23] which concerns structural perturbations

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[5] M. A. Ratner and R. D. Levine, *J. Am. Chem. Soc.*, **102**, 4898 (1980).

[6] R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

[7] H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **85**, 2544 (1963).

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[12] J. R. Murdoch, *J. Am. Chem. Soc.*, **105**, 2159 (1983).

[13] J. R. Murdoch, *J. Am. Chem. Soc.*, following paper in this issue.

[14] C. Eckart, *Phys. Rev.*, **35**, 1303 (1930).

[15] A. J. Kresge, *Chem. Soc. Rev.*, **2**, 475 (1973).

[16] J. L. Kurz, *Chem. Phys. Lett.*, **57**, 243 (1978).

[17] Eckart's function is given by

$$\Delta E^{\ddagger} = \Delta E e^x/(1 + e^x) + 4\Delta E_0^{\ddagger} e^x/(1 + e^x)^2$$

The barrier height is given by

$$E^{\ddagger} = \Delta E_0^{\ddagger} + \tfrac{1}{2}\Delta E + \Delta E^2/16\Delta E_0^{\ddagger}$$

The barrier position is given by $X^{\ddagger} = \ln (Z^{\ddagger}/(1 - Z^{\ddagger}))$, where $Z^{\ddagger} = {}^1/_2(1 + \Delta E/4\Delta E_0^{\ddagger})$.

[18] D. H. Aue and M. T. Bowers, *Gas Phase Ion Chem.*, **1**, 8 (1979).

[19] (a) J. R. Murdoch and D. E. Magnoli, Fifth IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, August, 1980; (b) J. R. Murdoch and D. E. Magnoli, Abstracts, Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 1980, No. PHYS-63, 64.

[20] B. Giese, *Angew. Chem., Int. Ed. Engl.*, **16**, 125 (1977).

[21] Examples include carbonyl addition and 2 + 4 cycloadditions where no simple analogy for the identity reactions exists. However, intrinsic barriers for such cases can be obtained in other ways: for example, the Marcus equation can be used to obtain an intrinsic barrier for any reaction by averaging the arithmetic and geometric means of the barriers in the forward and reverse directions. For reactions near thermoneutrality, the intrinsic barrier becomes the arithmetic mean of the barriers in the forward and reverse directions. Also, see ref 30.

[22] In general, any stationary point will suffice.

[23] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

[24] J. E. Leffler, *Science (Washington, D.C.)*, **117**, 340 (1953).

along the reaction coordinate in the limit of highly endothermic or exothermic reactions, and Leffler's principle,[24] which deals with differential energy changes along the reaction coordinate.

In spite of the success of Hammond's postulate and associated concepts, it has been apparent that structural perturbations in directions orthogonal to the reaction coordinate can often be significant.[2,3] The first indication of this comes from a suggestion made in 1936 by Hughes, Ingold, and Shapiro[25] in regard to S_N1 and S_N2 substitution reactions at carbon. Hughes, Ingold, and Shapiro considered the effect of a perturbation on two arbitrary points of a potential surface. If the two points are separated by an energy minimum and the energy of one point (relative to the other) is raised by a perturbation, then the position of the minimum shifts toward the lower point. The opposite behavior will be observed for two points separated by an energy maximum. The effect is based on the analogous behavior of a parabolic minimum or maximum when a linear perturbation is superimposed. The analogy with a parabola/linear perturbation is of interest if the potential surface in the vicinity of the transition state can be approximated as a hyperbolic paraboloid and if the change in relative energy along a line connecting two points separated in energy by δE, for example, can be taken to be a linear function of position between the two points. In 1967, Thornton[3a] formalized this approach by including a parabola and a linear perturbation for each internal degree of freedom associated with the potential surface. The two-dimensional version of this idea (a reaction coordinate and one orthogonal coordinate) has seen extensive qualitative use[3] for interpreting substituent effects on kinetic isotope effects and on barriers to nucleophilic substitution reactions, elimination reactions, carbonyl additions, proton transfer reactions, sigmatropic rearrangements, and Diels–Alder reactions. Although the basic idea seems to have clearly originated with Hughes, Ingold, and Shapiro in 1936, Thornton (1967),[3a] Harris and Kurz (1970),[3b] More O'Ferrall (1970),[1] Jencks (1972),[3c] Bruice (1976),[3e] Gajewski (1979),[3i] and others[3] have made their own important contributions and have popularized use of the two-dimensional potential surfaces which are currently known as More O'Ferrall plots.

In some recent publications appearing in this journal, it has been implied that More O'Ferrall plots are a "more rigorous" approach than the Marcus equation and that the More O'Ferrall plots are a "conceptual advance" because of the so-called perpendicular effects (i.e., substituent effects on coordinates orthogonal to the reaction coordinate). Such remarks are not well-founded, since it can be shown (vide infra) that the perpendicular effects included in the More O'Ferrall plots are associated with the intrinsic barrier term of Marcus' eq.[41] There have also been qualitative suggestions indicating certain similarities between the More O'Ferrall plot and the Marcus equation. For example, Jencks has noted that the magnitude of a shift in transition-state position is dependent on the curvature at the saddle point of the More O'Ferrall plot or on the magnitude of the "intrinsic barrier" of the Marcus equation,[3f] while Albery and Kreevoy have pointed out that the Marcus intrinsic barrier contains a sum of contributions arising from displacements along several orthogonal coordinates.[3g] However, the quantitative connection between the two approaches has never been detailed.

II. Expression for the Energy and Position of the Stationary Point

A. A Potential Energy Surface Function and Coordinates. The simplest potential surface exhibiting a stationary point with one negative second derivative and one positive second derivative is a hyperbolic paraboloid.[26] Such surfaces, or plane sections of such surfaces, have been considered by Thornton,[3a] Kurz,[16] Jencks,[3f] and Gajewski[3i] in connection with analyzing perpendicular and parallel substituent effects. It should be noted that while hyperbolic paraboloid surfaces give a stationary point corresponding to a transition state or stable intermediate, there is no stationary point for the reactants, products or for the two reference structures located at the ends of the perpendicular coordinate (Figures 1 and 2). Furthermore, when the coordinate axes are expressed in terms of Cartesian coordinates, such surfaces bear little resemblance to potential energy surfaces generated by ab initio techniques[27] or by empirical methods such as BEBO,[7] LEPS,[28] or diatomics-in-molecules.[29] Consequently, one could raise potentially serious objections as to whether the hyperbolic paraboloid, coupled with the linear perturbation, is an adequate basis for projecting the effects of perturbations on reactants, products, and the perpendicular reference structures (Figure 1) onto stationary points located in the central region of the surface. None of these potential problems have been dealt with in any detail in previous proposals concerning hyperbolic paraboloids as models for real potential energy surfaces.

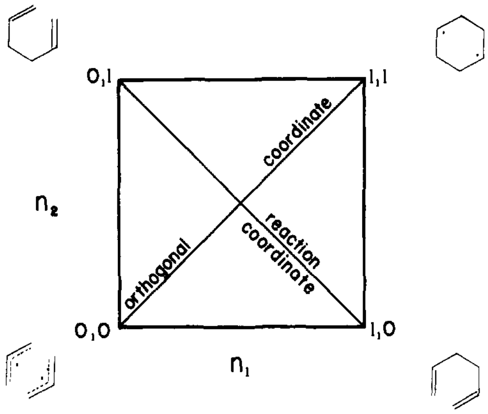

Figure 1. Translation of reaction coordinate/orthogonal coordinate axis to $n_1 = {}^1/_2$, $n_2 = {}^1/_2$. The illustrated structures are pertinent to a 3,3-sigmatropic shift. The reactants are located at (1,0), the products are located at (0,1). Bond breaking without simultaneous bond formation leads to the pair of allyl radicals at (0,0), while bond formation without simultaneous bond breaking leads to the cyclohexane diradical at (1,1).

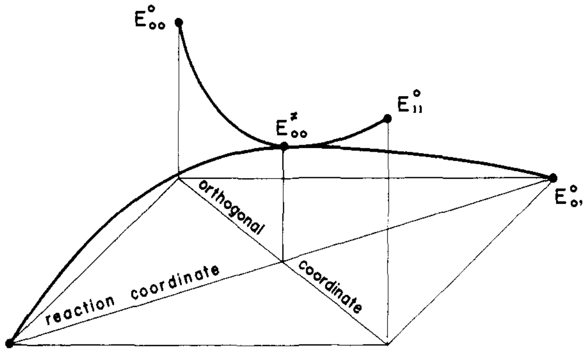

Figure 2. More O'Ferrall plot. When $E_{10}{}^\circ = E_{01}{}^\circ$ and $E_{00}{}^\circ = E_{11}{}^\circ$, the barrier is given by $E_{00}{}^\ddagger$ and the reaction coordinate corresponds to a straight line connecting (1,0) and (0,1). Total bond order is conserved (i.e., $n_1 + n_2 = 1$).

We[30] have examined these questions from both empirical and ab initio viewpoints. The lack of stationary points for the reactants, products, and perpendicular reference structures is not a serious problem, since many ab initio potential surfaces[27] also lack stationary points for these structures *when the surfaces are expressed*

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(25) E. D. Hughes, C. K. Ingold, and U. G. Shapiro, *J. Chem. Soc.*, 225 (1936).

(26) $Y = ax^2 - by^2 + cx + dy + e$

(27) C. F. Bender, S. V. O'Neil, P. K. Pearson, and H. F. Schaefer, III, *Science (Washington, D.C.)* **176**, 1412 (1972).

(28) (a) F. London, *Z. Elektrochem.*, **35**, 552 (1929); (b) S. Sato, *J. Chem. Phys.*, **23**, 592 (1955); (c) H. Eyring and M. Polanyi, *Z. Phys. Chem., Abt. B.* **12**, 279 (1931).

(29) (a) F. O. Ellison, *J. Am. Chem. Soc.*, **85**, 3540 (1963); (b) J. C. Tully, *J. Chem. Phys.*, 64, 3182 (1976).

(30) (a) J. R. Murdoch, D. E. Magnoli, and J. E. Donnella, James Flack Norris Award Symposium in Physical Organic Chemistry, 183rd Meeting of the American Chemical Society, Las Vegas, NV, March, 1982; (b) J. R. Murdoch and J. E. Donnella, *J. Am. Chem. Soc.*, in press.

in terms of bond-order coordinates[30] *rather than Cartesian coordinates.* Furthermore, after transformation from Cartesian to bond-order coordinates, certain ab initio and empirical surfaces bear a strong resemblance to hyperbolic paraboloids in many respects. This includes the areas near the stationary point as well as near the reactants, products, and perpendicular reference structures. The primary discrepancies from the hyperbolic paraboloid involve differences in the appearance of the contour lines, pronounced flattening of the region near the stationary point, and a tendency for the reaction coordinate to follow an S-shaped curve, rather than the straight line corresponding to bond-order conservation along the reaction coordinate or the arc-shaped curve observed when the perpendicular reference structures are at different energies (Figure 2). These differences are least important when the stationary point is in the central region of the surface ($n_1, n_2 \cong {}^1/_2$; see Figure 2) or when the stationary point is close to one of the four corners (0,0; 0,1; 1,0; 1,1). For certain reactions, the differences are insignificant regardless of where the stationary point is located. The departures of real potential surfaces from hyperbolic paraboloids are important, and it would be a mistake to simply cast them aside, particularly when kinetic isotope effects or geometries are important considerations. This work will be reported in detail in a subsequent paper[30b] and, along with the examples reported here, illustrates that in spite of certain discrepancies, hyperbolic paraboloids are not totally unreasonable as first- or zero-order approximations to real potential energy surfaces when the surfaces are expressed in terms of bond-order coordinates rather than Cartesian coordinates. Similar transformations have been made[31] by Morse[32] in solving for wave functions of vibrational oscillators and by Eckart[14] in solving quantum mechanical tunneling problems.

B. Hyperbolic Paraboloid Potential Surface and Bond-Order Coordinates. A general hyperbolic paraboloid surface can be expressed in terms of two orthogonal coordinates (x_o, y_o) which for the present problem (Figure 1) can be taken to be unit vectors parallel with the orthogonal and reaction coordinates, respectively.[33]

$$E = ax_o^2 - by_o^2 + cx_o + dy_o + e \qquad (5)$$

The origin of the (x_o, y_o) coordinate system is at $n_1 = {}^1/_2$; $n_2 = {}^1/_2$, and for $x_o, y_o = 0, -1/(2)^{1/2}$; $0, +1/(2)^{1/2}$; $-1/(2)^{1/2}, 0$; $+1/(2)^{1/2}, 0$, respectively, E takes on the values E_{10}, E_{01}, E_{00}, E_{11}, respectively, where E_{10} is the energy[34] of the reactants, E_{01} is the energy of the products, E_{00} is the energy of one perpendicular reference structure (Figures 1 and 2), and E_{11} is the energy of the second perpendicular reference structure. Furthermore, $E = E_0^\ddagger$ for $x_o, y_o = 0,0$ where $E_0^\ddagger$ is a constant for each surface, but may vary from one surface to another. These values for x_o, y_o, and E yield

$$a = E_{00} + E_{11} - 2E_0^\ddagger \qquad (6)$$

$$b = 2E_0^\ddagger - (E_{01} + E_{10}) \qquad (7)$$

$$c = \frac{E_{11} - E_{00}}{(2)^{1/2}} \qquad (8)$$

$$d = \frac{E_{01} - E_{10}}{(2)^{1/2}} \qquad (9)$$

$$e = E_0^\ddagger \qquad (10)$$

Noting that the (x_o, y_o) and (n_1, n_2) coordinate systems are rotated 45° with respect to one another, E can be expressed in terms of the bond-order coordinate axes (n_1, n_2), as in Figure 1:

$$E = \frac{a-b}{2}(n_2 - {}^1\!/_2)^2 + \frac{a-b}{2}(n_1 - {}^1\!/_2)^2 + (a+b)(n_1 - {}^1\!/_2)(n_2 - {}^1\!/_2) + (c+d)\frac{1}{(2)^{1/2}}(n_2 - {}^1\!/_2) + (c-d)\frac{1}{(2)^{1/2}}(n_1 - {}^1\!/_2) + e \qquad (11)$$

Setting $\mathrm{d}E^\ddagger/\mathrm{d}y_0 = 0$ and $\mathrm{d}E^\ddagger/\mathrm{d}x_0 = 0$,

$$(n_2^\ddagger - {}^1\!/_2) = \frac{d}{2(2)^{1/2}b} - \frac{c}{2(2)^{1/2}a} \qquad (12)$$

$$(n_1^\ddagger - {}^1\!/_2) = -\frac{d}{2(2)^{1/2}b} - \frac{c}{2(2)^{1/2}a} \qquad (13)$$

where $n_2^\ddagger$ and $n_1^\ddagger$ represent the coordinates of the stationary point in terms of a, b, c, d (eq 6–9).[35a]

Substituting eq 12 and 13 into eq 11 gives the energy of the stationary point

$$E^\ddagger = \frac{(E_{01} - E_{10})^2}{8(2E_0^\ddagger - (E_{01} + E_{10}))} - \frac{(E_{11} - E_{00})^2}{8(E_{00} + E_{11} - 2E_0^\ddagger)} + E_0^\ddagger \qquad (14)$$

Following Thornton[3a] on adding a linear perturbation to the potential surface, changes in the energies of the four corner points (Figures 1–3) will alter $E_0^\ddagger$ according to[35b]

$$E_0^\ddagger = E_{00}^\ddagger + \frac{E_{01} + E_{10}}{2} - \frac{E_{01}^\circ + E_{10}^\circ}{2} + \frac{E_{11} + E_{00}}{2} - \frac{E_{11}^\circ + E_{00}^\circ}{2} \qquad (15)$$

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(31) Setting $n = e^{-a(r-r_0)}$, the Morse function (ref 32) can be expressed as $E = D_1[n^2 - 2n]$.

(32) P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).

(33) The cross term has been omitted. Note that it vanishes upon a 45° rotation: $f(x_0)(y_0) = f(m_2 \sin\theta + m_1 \cos\theta)(-m_1 \sin\theta + m_2 \cos\theta) = f(m_1 m_2[\cos^2\theta - \sin^2\theta] - m_1^2(\cos\theta \sin\theta) + m_2^2(\sin\theta \cos\theta)) = [f(\mathrm{m}_2^2 - \mathrm{m}_1^2)]^1/_2$. The effect of including the cross term $x_o y_o$ is to modify the quadratic coefficients of m_1 and m_2. Including the $x_o y_o$ term modifies the nonlinear terms of eq 14 somewhat. Equations 12 and 13 become (note: $m_i = n_i^\ddagger - {}^1/_2$)

$$(n_2^\ddagger - {}^1\!/_2) = (2)^{1/2}[ad - {}^1\!/_2fc - {}^1\!/_2fd - bc]/[4ab + f^2] \qquad (12a)$$

$$(n_1^\ddagger - {}^1\!/_2) = (2)^{1/2}[-ad + {}^1\!/_2fc - {}^1\!/_2fd - bc]/[4ab + f^2] \qquad (13a)$$

Equation 14 becomes

$$E^\ddagger = \frac{4aA^2}{D^2} - \frac{4bB^2}{D^2} + \frac{4ABf}{D^2} + \frac{2cB + 2dA}{D} + e \qquad (14a)$$

$$A = ad - {}^1\!/_2fc \qquad (14b)$$

$$B = -(bc + {}^1\!/_2fc) \qquad (14c)$$

$$D = 4ab + f^2 \qquad (14d)$$

(34) Following the theoretical treatment given earlier (ref 4j,l; 11–13), the surface is presented in terms of E (electronic energy where $E = T + V_{\mathrm{ne}} + V_{\mathrm{ee}} + V_{\mathrm{nn}}$). Note that zero-point energies, enthalpy corrections, and entropy contributions are not specifically included, although empirical considerations (e.g., ref 4j) suggest that Marcus-type relationships may still operate for ΔH° and ΔG°.

(35) (a) Note that the first term (due to energy differences between reactants and products) in eq 12 and 13 changes n_1 and n_2 in opposite directions, while the second term (due to energy differences between the two perpendicular reference structures) changes n_1 and n_2 in the same direction. For $c = 0.0$, bond-order conservation operates. (b) Thornton's treatment employs a symmetric inverted parabola with a stationary point (e.g., $E_{00}^\ddagger$) at $n = {}^1/_2$ plus a linear perturbation with a value of ΔE at $n = 1$. The total energy at $n = {}^1/_2$ is given by $E({}^1/_2) = E_{00}^\ddagger + {}^1/_2\Delta E$, so that half of the linear perturbation contributes to E at $n = {}^1/_2$. In two dimensions, Thornton would have two linear perturbations, one corresponding to the reaction coordinate and the other corresponding to the orthogonal coordinate. At $n = {}^1/_2$, half of the perturbation adds to $E_{00}^\ddagger$ to give $E({}^1/_2)$. In eq 15, the term corresponding to Thornton's ${}^1/_2\Delta E$ is ${}^1/_2[E_{01} + E_{10} - E_{01}^\circ - E_{10}^\circ]$ while the term corresponding to half of the orthogonal perturbation is ${}^1/_2[E_{11} + E_{00} - E_{11}^\circ - E_{00}^\circ]$. Note that the quadratic surface used in the present treatment has five parameters and that these are defined by the four values of the corner points and the constraint that plane sections which connect the diagonal corner points of the parabolic surface will appear as symmetric parabolas plus a sum of linear perturbations which are associated with each orthogonal coordinate, just as in Thornton's model. Gajewski has used an alternate constraint which minimizes the least-squares deviations between the calculated and observed barriers (J. J. Gajewski, private communication). One effect of the J.J.G. constraint is that the parallel/perpendicular substituent effects are roughly one half of those in the Marcus/Thornton approach used here. A detailed analysis will be given elsewhere.

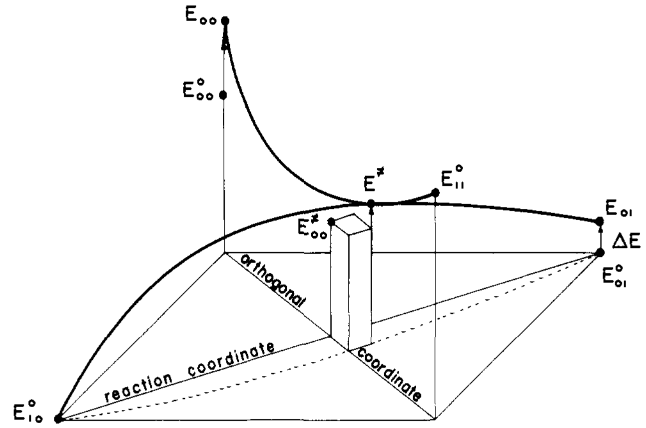

Figure 3. Effect of a perturbation on the energy of the transition state and on the reaction coordinate. Simultaneously raising the energy of the products relative to the reactants and increasing E_{00} shifts the transition-state structure toward products and toward the "perpendicular" reference structure at (1,1). The energy of the transition state increases from $E_{00}^{\ddagger}$ to $E^{\ddagger}$. The reaction coordinate deviates from the bond-order conservation path according to the dashed line.

where $E_{00}^{\ddagger}$ equals $E_0^{\ddagger}$ for $E_{01} = E_{10} = E_{01}^{\circ} = E_{10}^{\circ}$ and $E_{11} = E_{00} = E_{00}^{\circ} = E_{11}^{\circ}$. The relationship between E_{11}, E_{00}, E_{01}, E_{10} and E_{11}°, E_{00}°, E_{01}°, E_{10}° is illustrated in Figures 2 and 3, and it should be noted that since E_{11}°, E_{00}°, E_{01}°, E_{10}° are simply reference points their values can be chosen arbitrarily or to reflect physical quantities appropriate to an actual reaction.

The relationship between eq 14 and 15 and Marcus' equation can be seen by setting E_{10} (energy of reactants), E_{01}°, and E_{10}° to zero,[36] by setting $E_{00}^{\ddagger} = \Delta E_{00}^{\ddagger}$ and $\Delta E = E_{01} - E_{10} = E_{01}$, and by substituting eq 15 into eq 14:

$$\Delta E^{\ddagger} = \frac{\Delta E^2}{16(\Delta E_{00}^{\ddagger} + \tfrac{1}{2}[E_{11} + E_{00} - E_{11}^{\circ} - E_{00}^{\circ}])} + \tfrac{1}{2}\Delta E + \Delta E_{00}^{\ddagger} + \tfrac{1}{2}[E_{11} + E_{00} - E_{11}^{\circ} - E_{00}^{\circ}] - \frac{(E_{11} - E_{00})^2}{16(\tfrac{1}{2}[E_{11}^{\circ} + E_{00}^{\circ}] - \Delta E_{00}^{\ddagger} - \tfrac{1}{2}\Delta E)} \qquad (16)$$

Rewriting eq 1 in terms of ΔE, etc. and comparing terms, it can be seen that Marcus' intrinsic barrier is given by

$$\Delta E_0^{\ddagger} = \Delta E_{00}^{\ddagger} + \tfrac{1}{2}[E_{11} + E_{00} - E_{11}^{\circ} - E_{00}^{\circ}] \qquad (17)$$

and that the last term on the rhs of eq 16 represents nonadditive contributions from energy differences between the perpendicular reference structures.

$$\Delta E^{\ddagger} = \Delta E^2/16\Delta E_0^{\ddagger} + \tfrac{1}{2}\Delta E + \Delta E_0^{\ddagger\prime} \qquad (18)$$

$$\Delta E_0^{\ddagger\prime} = \Delta E_0^{\ddagger} - (E_{11} - E_{00})^2/16[\tfrac{1}{2}(E_{11}^{\circ} + E_{00}^{\circ}) - \Delta E_{00}^{\ddagger} - \tfrac{1}{2}\Delta E] \qquad (19)$$

In the limit of small changes in E_{11} and E_{00}, $\Delta E_0^{\ddagger} = \Delta E_0^{\ddagger\prime}$, and eq 18 reduces to Marcus' equation. Two important points emerge: (1) The energies of the perpendicular reference structures enter into the intrinsic barrier terms. (2) There are two intrinsic barrier terms. One ($\Delta E_0^{\ddagger}$) depends on $\Delta E_{00}^{\ddagger}$ and the energies of the perpendicular reference structures and the other ($\Delta E_0^{\ddagger\prime}$) depends on $\Delta E_{00}^{\ddagger}$ and the energies[36] of all four corner points. Both $\Delta E_0^{\ddagger}$ and $\Delta E_0^{\ddagger\prime}$ are expected to vary from reaction to reaction.

III. Application to 3,3-Sigmatropic Shifts

Gajewski has provided an extremely interesting application of the parallel/perpendicular perturbation effect in a series of 3,3-sigmatropic rearrangements.[3i] His novel treatment is based on a simplified form of eq 11 which does not include the two quadratic terms in $(n_2 - {}^1/_2)^2$ and $(n_1 - {}^1/_2)^2$. Partly because of this omission, it is necessary to introduce an arbitrary scaling factor[3i,37] for the energies of the two perpendicular reference structures. Gajewski has compiled data from the literature, and these have been used to calculate intrinsic barriers and overall barriers[38] for various 3,3-shifts (Table I). $\Delta E_{00}^{\ddagger}$ (43 kcal) is obtained from the 1,5-hexadiene reaction and is used without change for the remainder of the reactions. The standard deviation between calculated and experimental barriers is about 3 kcal and is essentially identical with Gajewski's deviation obtained with one adjustable parameter. Considering that the energies of the perpendicular reference structures are crude estimates in most cases, the overall agreement seems satisfactory.[39]

IV. Application to $[2_s + 4_s]$ Cycloaddition Reactions

Gajewski has also applied the parallel/perpendicular idea to Diels–Alder reactions between cyclopentadiene and cyano-substituted ethylenes. Intrinsic barriers and calculated values of $\Delta E^{\ddagger}$ (eq 18 and 19) for these reactions appear in Table II. The standard deviation between calculated and experimental barriers is about 1.3 kcal over a range of $\Delta E^{\ddagger}$ from 29 to 14 kcal. The value for $\Delta E_{00}^{\ddagger}$ has been taken from the acrylonitrile addition reaction and used without change for the remaining reactions. The agreement between calculated barriers and experimental barriers seems reasonable[39] in view of the assumption that all reactions have the same ΔG (−20 kcal) and that the α-cyano radical resonance energy (9 kcal) is strictly additive.[40]

V. Discussion

A. Intrinsic Barrier for the Hydrocarbon Reactions—Orbital Symmetry Constraints.

$\Delta E_{00}^{\ddagger}$ can be interpreted as the intrinsic barrier associated with a convenient reference reaction, and in the present case this is chosen to be 1,5-hexadiene for the 3,3-shift and ethylene/cyclopentadiene for the 2 + 4 cycloaddition. The fact that $\Delta E_{00}^{\ddagger}$ is relatively close for the two reactions (43 vs.38 kcal) is striking as is the fact that $\Delta E_{00}^{\ddagger}$ is relatively constant within each class of reaction. It is possible that a significant portion of the deviations between calculated and observed barriers can be attributed to nonconstant $\Delta E_{00}^{\ddagger}$ values for each reaction.

$\Delta E_{00}^{\ddagger}$ represents the barrier for a hypothetical thermoneutral reference reaction where the two perpendicular structures are of

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[36] Some caution needs to be exercised in using eq 16 since the last term involving $(E_{11} - E_{00})^2$ depends on how the change in ΔE takes place. A somewhat different surface will be obtained if the reactants are defined as the energy zero and the products raised in energy by ΔE than if the energy of the products is set to zero and the reactants lowered in energy by ΔE. Both surfaces involve the same change in ΔE, but note that the relationship between the parallel reference structures and the reactants or products is different in the two cases. This dependency of the potential surface on ΔE as well as the differences $E_{01} - E_{00}$ and $E_{01} - E_{11}$ is even more pronounced for Gajewski's surface (ref 3i). The fact that different surfaces may correspond to the same value of ΔE is not a violation of microscopic reversibility, as suggested in ref 3i, and has precendents in other empirical potential energy surfaces such as BEBO,[7] LEPS,[28] and DIM.[29] For example, in the BEBO surface,[7] $E = V_A(1 - n)^{P_A} + V_B(n)^{P_B}$. For $P_A \neq P_B$, $V_A = V_A^{\circ} + \delta$ and $V_B = V_B^{\circ}$ gives $\Delta E = V_A - V_B = V_A^{\circ} + \delta - V_B^{\circ}$ which is the same ΔE given by $V_A = V_A^{\circ}$ and $V_B = V_B^{\circ} - \delta$. However, $V_A = V_A^{\circ} + \delta$; $V_B = V_B^{\circ}$ gives a different surface than $V_A = V_A^{\circ}$; $V_B = V_B^{\circ} - \delta$ and the values of n and E at the stationary point are slightly different. The main point is that ΔE, $\Delta E_0^{\ddagger}$ are sufficient for defining the parabolic surface (eq 5) only to the extent that the last term of eq 16 is negligible. In other cases, energies, enthalpies, or free energies of formation (or other measure of energy relative to the same reference for all reactions, e.g., free atoms) can be used in eq 14 and 15 to give a unique surface for each reaction. It should also be noted that Marcus' equation cannot be used for $|\Delta E| > 4\Delta E_0^{\ddagger}$, and analogous limits will occur for this quadratic surface. See ref 41 for a discussion of these thermodynamic limits.

[37] In Gajewski's original treatment, the scaling factor, P, is introduced by having the products at coordinates (P,P) instead of (1,1). An alternative interpretation is to replace E_{00} and E_{11} with $E_{00}P$ and $E_{11}P$.

[38] Equation 16 has been used as a simple expedient since for most of these examples, the differences mentioned in ref 36 are modest. Equations 14 and 15 can be used as an alternative if total energies, heats of formation, energies of atomization, etc., are available.

[39] Gajewski's surface exhibits the feature noted in footnote 36: two different surfaces are obtained when the energy of the products is raised x kcal or when the energy of the reactants is lowered x kcal. The discrepancies between the observed $\Delta G^{\ddagger}$'s and those calculated from Gajewski's equation increase somewhat if the definitions of reactants and products are reversed: σ = 5.3 kcal for 3,3-sigmatropic shifts, and σ = 5.6 kcal for 2 + 4 cycloadditions.

[40] The deviations are consistent with a leveling effect in the resonance energy per nitrile group for tri- and tetracyanoethylenes.

Table I. Application of Marcus' Equation to 3,3-Sigmatropic Shifts

	$\Delta E_{\text{obsd}}^{\ddagger\,a}$	$\Delta E_{\text{calcd}}^{\ddagger\,b}$	$\Delta E_{NT}^{\ddagger\,c,d}$	$\Delta E_{AT}^{\ddagger\,e}$	$\Delta E_{NK}^{\ddagger\,f}$	$\Delta E_{AK}^{\ddagger\,g}$	$E_{00}^{a,h}$	$E_{11}^{a,h}$	ΔE^{a}	$(n_2 - {}^1/_2)_T{}^i$	$(n_2 - {}^1/_2)_K{}^j$	$(n_2 - {}^1/_2)^k$
1,5-hexadiene	41	40.9	0.0	0.0	−0.1	41.0	57	53	0.0	0.00	0.04	0.04
2-phenyl-1,5-hexadiene	35.5	34.5	0.0	0.0	−1.0	35.5	57	42	0.0	0.00	0.13	0.13
2,5-diphenyl-1,5-hexadiene	31	27.0	0.0	0.0	−3.0	30.0	57	31	0.0	0.00	0.23	0.23
3,3-dicyano-1,5-hexadiene	32	27.8	0.04	−2.3	−1.0	31.0	37	53	−4.5	−0.02	−0.23	−0.25
3,4-dimethyl-1,5-hexadiene (threo)	39	36.8	0.03	−2.3	0.0	39.0	53	53	−4.5	−0.01	0.00	−0.01
3,4-diphenyl-1,5-hexadiene (threo)	31	26.5	0.04	−2.3	−1.2	30.0	35	53	−4.5	−0.02	−0.14	−0.16
cis-1,2-divinylcyclobutane	28	22.4	0.68	−9.5	−1.8	33	34	60	−19	−0.07	−0.14	−0.21
allyl vinyl ether	33	27.9	0.5	−8.5	−0.1	36	47	53	−17	−0.06	−0.03	−0.09
allyl phenyl ether	42	43.9	0.04	2.5	−2.6	44	47	69	+5	0.01	−0.24	−0.23
allyl acetate	45	44.5	0.00	0.0	−1.0	45.5	52	67	0	0.00	−0.13	−0.13
cis-1,2-divinylcyclopropane	21	20.0	0.8	−10.0	−0.8	30.0	35	53	−20	−0.08	−0.09	−0.17
allyl silyl enol acetate	<25	26.6	0.7	−10.0	−0.1	36.0	47	53	−20	−0.07	−0.03	−0.10
3-oxyanion-1,5-hexadiene	~26	24.9	0.7	−9.5	−0.3	34.0	43	53	−19	−0.07	−0.05	−0.12

[a] Reference 3i (cited from literature), kcal. Standard deviation = 3.1 kcal. [b] Equations 18 and 19. [c] $\Delta E_{\text{calcd}}^{\ddagger}$ is dissected into four contributions: $\Delta E_{NT}^{\ddagger}$, $\Delta E_{AT}^{\ddagger}$, $\Delta E_{NK}^{\ddagger}$, $\Delta E_{AK}^{\ddagger}$. [d] $\Delta E_{NT}^{\ddagger} = \Delta E^2/16\Delta E_0^{\ddagger}$. [e] $\Delta E_{AT}^{\ddagger} = {}^1/_2\Delta E$. [f] $\Delta E_{NK}^{\ddagger} = (E_{11} - E_{00})^2/16[{}^1/_2(E_{11}{}^\circ + E_{00}{}^\circ) - {}^1/_2\Delta E]$. [g] $\Delta E_{AK}^{\ddagger} = \Delta E_{00}^{\ddagger} + 0.5[E_{11} + E_{00} - E_{11}{}^\circ - E_{00}{}^\circ]$. [h] E_{00} is the energy of two substituted allyl radicals; E_{11} is the energy of substituted cyclohexyl-1,4-diyl. [i] $(n_2 - {}^1/_2)_T = d/((2)^{1/2}2b)$, eq 12. [j] $(n_2 - {}^1/_2)_K = -c/((2)^{1/2}2a)$, eq 12. [k] $(n_2 - {}^1/_2) = (n_2 - {}^1/_2)_K + (n_2 - {}^1/_2)_T$, eq 12.

Table II. Application of Marcus' Equation to 2 + 4 Cycloadditions

cyclopentadiene plus:	$\Delta E_{\text{obsd}}^{\ddagger\,a}$	$\Delta E_{\text{calcd}}^{\ddagger\,b}$	$\Delta E_{NT}^{\ddagger\,c,d}$	$\Delta E_{AT}^{\ddagger\,e}$	$\Delta E_{NK}^{\ddagger\,f}$	$\Delta E_{AK}^{\ddagger\,g}$	$E_{00}^{a,h}$	$E_{11}^{a,h}$	ΔE^{a}	$(n_2 - {}^1/_2)_T{}^i$	$(n_2 - {}^1/_2)_K{}^j$	$(n_2 - {}^1/_2)^k$
ethylene	~30	28.9	0.7	−10	0.0	38.2	40	40	−20	−0.07	0.00	−0.07
acrylonitrile	24.0	24.0	0.7	−10	−0.4	33.7	40	31	−20	−0.07	−0.10	−0.17
fumaronitrile	21.3	20.1	0.9	−10	0.0	29.2	31	31	−20	−0.09	0.00	−0.09
maleonitrile	21.1	20.1	0.9	−10	0.0	29.2	31	31	−20	−0.09	0.00	−0.09
1,1-dicyanoethylene	17.8	18.3	0.9	−10	−1.7	29.2	40	22	−20	−0.09	−0.19	−0.27
1,1,2-tricyanoethylene	16.3	15.3	1.0	−10	−0.4	24.7	31	22	−20	−0.10	−0.10	−0.20
1,1,2,2-tetracyanoethylene	13.9	11.4	1.2	−10	0.0	20.2	22	22	−20	−0.12	0.00	−0.12

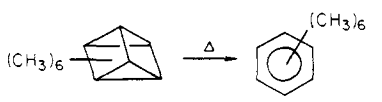
[a–g] See Table I. [h] E_{00} = energy of structure formed by bond formation across C_2 of ethylene and C_1 of cyclopentadiene. E_{11} = energy of structure formed by bond formation across C_1 of ethylene and C_4 of cyclopentadiene. [i–k] See Table 1.

equal energy. Orbital symmetry constraints do not exert an appreciable influence on ΔE for the overall reaction, but should be a primary consideration in determining the relative magnitudes of $\Delta E_{00}^{\ddagger}$ for various reactions. Symmetry-allowed processes would be expected to have smaller values of $\Delta E_{00}^{\ddagger}$ compared to analogous symmetry-disallowed reactions. Barriers for both classes of reaction could be modified by changes in energy of the perpendicular structures and by changes in ΔE (Figure 2).

B. Overriding Orbital Symmetry Constraints. 1. Substituent Effects on the Intrinsic Barrier. One interesting implication of eq 18 and 19 is that stabilization of the perpendicular structures relative to the reactants and products will reduce the intrinsic barrier for the reaction (Figure 2). More specifically, if each perpendicular structure is stabilized to the same extent, then the intrinsic barrier will be reduced by the same amount. In addition, if one structure is stabilized by an additional amount, then the intrinsic barrier is further reduced by half of this increment. For large energy changes in the perpendicular structures, the nonadditive term of eq 19 may be important.

The relative response of the perpendicular structures to substituent effects has an important bearing on the concerted/nonconcerted nature of sigmatropic shifts and cycloadditions. If one of these structures is stabilized to a greater extent, the transition state will shift toward the more stable of the perpendicular structures. According to eq 19, the response of the intrinsic barrier lags behind the stabilization of the perpendicular structure, so that for sufficiently large perturbations, the transition state energy will approach the energy of the more stable perpendicular structure and the nonconcerted pathway may be energetically competitive with the concerted process. When both perpendicular structures are stabilized relative to products and reactants, the transition state tends to remain in the middle portion of the potential surface, and the intrinsic barrier for the concerted process is reduced. Stabilization of the perpendicular structures raises the interesting possibility of overriding orbital symmetry constraints by lowering the intrinsic barrier for reaction. The intrinsic barrier for the ethylene/cyclopentadiene reaction (Table II) is about 38 kcal and is reduced by about 18 kcal after replacement of the four hydrogens of ethylene with four cyano groups. Stabilization of the perpendicular structures might also be achieved by complexation with Lewis acids[41] or transition metals,[42] and it is not difficult to imagine situations where the stabilization would be sufficient to lower the transition state to the point where the reaction proceeds through one or more intermediates. Baldwin[43] has reviewed several examples of symmetry-disallowed reactions which proceed with thermally accessible barriers. In each case, the perpendicular reference structures, radicals formed by cleavage of C–C σ or π bonds, are stabilized by extended π systems. Another possible mechanism for intrinsic barrier stabilization is *subadjacent* orbital control which has been proposed by Berson[44] in order to account for facile, 1,3-sigmatropic shifts (suprafacial/retention) which are symmetry-forbidden reactions.

2. Thermodynamic Substituent Effects. Another mode of reducing the barrier of the overall reaction is the incorporation of a favorable change in $\Delta E°$ or $\Delta G°$. An interesting example is the conversion of hexamethylprismane to hexamethylbenzene which is a symmetry-forbidden process. The reaction is ~90 kcal[45] downhill thermodynamically and has a barrier of 33 kcal. By use of Marcus' equation, the intrinsic barrier (i.e., the barrier for the hypothetical thermoneutral isomerization) is about 71 kcal,[21] and so the 90 kcal of exothermicity corresponds to 38 kcal of stabilization for the transition state. Note that the overall barrier of 33 kcal is comparable to the some of the barriers for the "allowed" 3,3-sigmatropic shifts. It is also significant that the intrinsic barrier for this thermally "forbidden" reaction is about 30 kcal higher than the intrinsic barriers (Tables I and II) for the 3,3-shift (1,5-hexadiene) and the 2 + 4 cycloaddition (ethylene/cyclopentadiene). The cycloadditions reported in Table II are downhill by 20 kcal, and about half of this is involved in stabilization of the transition state (see Table II). Similar effects can be noted for the 3,3-shifts seen in Table I.



C. Hughes–Ingold–Shapiro Effect. An Interpolation Scheme. The HIS effect is basically an interpolation scheme where perturbations to energies of four reference structures propagate linearly over a quadratic surface. The four structures need not be stable intermediates, but experimental determination of their response to perturbations is certainly simplified if this is the case. As mentioned earlier, it has been found[30] that the quadratic approximation is not bad as long as the surfaces are expressed in bond-order coordinates. Higher order terms are significant, and the consequences for predictions based on the simple parabolic approximation will be detailed elsewhere.[30b]

The linear propagation of substituent effects on the reference structures is also an assumption which has been tested in some detail.[30] By following the energy change along the reaction coordinate for certain ab initio SCF surfaces, it has been found that ΔE propagates along the reaction coordinate as a sigmoid function which is rather close to linear. Thus, the two major assumptions of the present paper, as well as previous work,[16,30,46] have been shown to be qualitatively sound on an empirical basis. It should also be mentioned that Dunn[46] has used an interpolation scheme where the edges of the surface are defined as fourth-order polynomials, and the center portion of the surface is constructed by interpolation from the opposing edges.

D. Intrinsic Barriers and Potential Energy Surfaces. The intrinsic barrier is rapidly becoming the focal point for studies of substituent effects on reaction rates[4,30] and is an essential part of the comparison of barriers of reactions of different thermodynamics.[4,30] An important result of the present paper is that the Marcus equation can now be applied to pericyclic reactions (as well as group transfer processes[4]), and consequently, intrinsic barriers can be obtained from $\Delta E^{\ddagger}$ and ΔE without reference to the details of the potential energy surface and without explicit recognition of the perpendicular reference structures (section V.B.1 and ref 30). On the other hand, the link between the More O'Ferrall plot and Marcus equation permits interpretation of the intrinsic barrier in terms of substituent effects on specific structures[47] in analogy with the intrinsic barriers derived[4g–k,6] from the Marcus equation and identity barriers of group transfer reactions. Consequently, the More O'Ferrall plot and the Marcus equation are two highly complementary and qualitatively equivalent approaches for expressing the effects of substituents on reaction barriers.

The treatment of these rather remarkable phenomena is also proceeding from a more rigorous and fundamental direction. In

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[47] The More O'Ferrall plot has generally been implemented with structures of "real" compounds or intermediates representing the corner points. An analogous method has recently been popularized (ref 47a,b) and is based on valence bond configurations (or resonance forms) which serve as the reference structures. Substituent effects may alter the relative energies of the configurations, and this in turn will affect the relative mixing of each valence bond configuration into the total wave function for a specific nuclear configuration on the potential surface. Changes in the relative mixing of the valence bond configurations can result in perturbations to the energy, nuclear geometry, charge distribution, etc. at the transition state. The MOF plot and the configuration-mixing model are similar in that they both give qualitative predictions concerning energy (higher vs. lower) and geometry (shorter bond length vs. longer bond length) as a function of substituents on reference structures (MOF) or valence bond configurations (ref 47a,b). A possible significant difference between the two methods is whether the reference structures are actual energy states of a particular nuclear configuration or valence bond configurations whose combination approximates the real energy states of a system. Even this distinction is somewhat hazy. For more detail, see (a) N. D. Epiotis, "Theory of Organic Reactions", Springer-Verlag, Heidelberg, 1978. (b) S. S. Shaik and A. Pross., *J. Am. Chem. Soc.*, **104**, 2708 (1982). Recognition of multiple electronic states may be important in the use of MOF plots, particularly when the states are close in energy (see comments in footnote *w* of Table I in ref 3i).

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previous papers,[11] a theory of nuclear substitution has been developed with the aim of providing a quantum mechanically sound framework for interpreting changes in molecular properties in terms of molecular structure. At present, this theory has been carried out to first-order wave function corrections (at the Hartree–Fock level), and a number of established chemical concepts have been shown to follow analytically from the first-order treatment. These include Benson's equivalent group schemes,[8] Pauling's covalent radii and electronegativity relationships,[48,49] free energy relations[49] such as the Hammett[10] and Drago equations,[50] and various rate–equilibrium relationships[12] including the Marcus equation.[2,4c] Preliminary results indicate that behavior derivable from parabolic/linear interpolation models is also closely associated with first-order perturbations, and consequently, this aspect, as well as extension to higher-order perturbations, is undergoing close examination.

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Barrier Heights and the Position of Stationary Points along the Reaction Coordinate

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Abstract: Miller has derived a remarkably simple relationship for predicting the barrier position along a reaction coordinate in terms of the reaction thermodynamics (ΔE) and the barrier height ($\Delta E^{\ddagger}$). This relationship correlates very well with a wide variety of ab initio and empirical potential energy surfaces, and these correlations have prompted an examination of the conditions leading to Miller's result. It is shown that Miller's conditions alone (some properties of double-knot spline functions, arc-length minimization) are *not* sufficient, but that a scaled symmetry relationship (plus Miller's conditions) is sufficient. Miller's result has been obtained by using different spline functions to represent different sections of the reaction coordinate, and it would be of general interest to determine whether the scaled symmetry relationship can be observed for nonspline functions which span the entire reaction coordinate. By use of a general reaction coordinate function, $E(X) = {}^1/_2\Delta E(1 + h_1(X)) + \Delta E_0{}^{\ddagger}(1 - h_2(X))$, it is found ($\Delta E \neq 0$) that a necessary and sufficient condition for the scaled symmetry relationship is $h_2(X) = h_1(X)^2$. It is also found that the barrier height follows the Marcus equation, and deviations from the Marcus equation can be understood in terms of deviations from the "square" relationship ($h_2 = h_1{}^2$). The present work emphasizes that the Marcus equation does *not* depend on specialized assumptions such as intersecting parabolas, inverted-parabola-plus-linear-perturbation, intersecting Morse functions, etc., but derives from a more general relationship (i.e., the scaled symmetry relationship or equivalently, the "square" relationship: $h_2 = h_1{}^2$). It is shown that the scaled symmetry relationship follows from a second-order expansion of the reaction coordinate in terms of suitable functions (e.g., a Fourier series or bond order). It is found that for $h_2 = h_1{}^2$, the barrier position ($X^{\ddagger}$) is dependent on the degree of nonlinearity in $h_1(X)$. For example, the sigmoid function, $h_1(X) = X^p - (1 - X)^p/[X^p + (1 - X)^p]$, leads to the Marcus relationship for the barrier position ($X^{\ddagger} = {}^1/_2 + \Delta E/8\Delta E_0{}^{\ddagger} = [1 + (1 - \Delta E/\Delta E^{\ddagger})^{1/2}]^{-1}$) for $p = 1$ and to the Miller relationship ($X^{\ddagger} = [2 - \Delta E/\Delta E^{\ddagger}]^{-1}$) for $p = {}^1/_2$. The scaled symmetry relationship emphasizes the relationship between h_2 and h_1, rather than the specific form of the barrier function, as the key factor in governing the response of the barrier position and height toward changes in the overall thermodynamics of a reaction. The present results provide a sound theoretical foundation for extending the application of Marcus-like expressions from electron, proton, and group transfers to *all* one-step reactions, including pericyclic processes, carbonyl additions, fragmentations, cheletropic reactions, conformational equilibria, isomerizations, and so forth.

I. Introduction

Position of Stationary Points on Potential Energy Surfaces. Recently, Miller[1] proposed a simple relationship for predicting the barrier position along the reaction coordinate, and his proposal was tested against other methods[2-5] of computing the barrier position. Miller concluded that his equations compare favorably with "the best of the methods for computing the barrier position", and this includes the ab initio approaches. Miller's relationship is simple and predicts that the barrier position ($X^{\ddagger}$) depends *only* on the height of the barrier ($\Delta E^{\ddagger}$) and the energy difference between products and reactants (ΔE):

$$X^{\ddagger} = \frac{1}{2 - \Delta E/\Delta E^{\ddagger}} \tag{1}$$

Miller derived this relationship by representing the reactant and product sides of the reaction coordinate by two separate spline functions (double-knot spline functions, DKSF) which are joined smoothly at the energy maximum. Miller's treatment leaves the choice of function for the splines completely open but imposes several constraints on the parameters so that the barrier function will have derivatives of zero at the initial and final points ($X = 0$, $X = 1$, respectively) and at the transition state ($X = X^{\ddagger}$). The values of the barrier function, $E(X)$, are constrained to pass

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