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Application of Marcus-like Equations to Group-Transfer Reactions. A Theoretical Test of Intrinsic Barrier Additivity and the "Square" Relationship

Jane Donnella and Joseph R. Murdoch*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received September 17, 1982*

Abstract: In previous work, it has been shown that a reaction coordinate can be described in terms of the general function $E(X) = \Delta E_0^\ddagger[1 - h_2(X)] + {}^1/_2\Delta E[1 + h_1(X)]$ where $\Delta E_0^\ddagger$ is the intrinsic barrier, ΔE is the energy change between reactants and products, and $h_1(X)$ and $h_2(X)$ are odd and even functions of the displacement (X) along the reaction coordinate. It has also been shown that the Marcus equation for the barrier height ($\Delta E^\ddagger = \Delta E_0^\ddagger + {}^1/_2\Delta E + \Delta E^2/16\Delta E_0^\ddagger$) results from the condition $h_2(X) = h_1(X)^2$ (i.e., the "square" relationship). In most applications of the Marcus equation, $\Delta E_0^\ddagger$ for a cross reaction (e.g., A–B + C → A + B–C) has been taken as the average of the two barriers for corresponding identity reactions (e.g., A–B + A → A + B–A and C–B + C → C + B–C). In this paper, the first test of intrinsic barrier additivity and the "square" relationship is made through the use of SCF calculations. It has been found that $\Delta E_0^\ddagger$ for the cross reaction (e.g., F–H + $^-$OH → F$^-$ + H–OH) is often close (within 0.5 kcal) to the average barrier (or well depth) of the corresponding identity reactions (e.g., F–H + $^-$F → F$^-$ + H–F and HO–H + $^-$OH → HO$^-$ + H–OH), while in other cases (Cl–H + $^-$OH → Cl$^-$ + H–OH), large deviations (6 kcal) from intrinsic barrier additivity are observed. It is also shown that the "square" relationship holds only when the position ($X^\ddagger$) of the energy maximum or minimum along the reaction coordinate is near 0.0, 0.5, or 1.0. For other values of $X^\ddagger$, quartic terms make substantial contributions (i.e., $h_2 = c_2h_1^2 + c_4h_1^4$), and it is significant that higher order terms are almost negligible. Preliminary results suggest that intrinsic barrier nonadditivity may be accounted for in terms of a generalized nonadditivity relationship, similar to a special case employed by Pauling to describe nonadditivity in diatomic molecules. The fact that h_2 is dominated by square and quartic terms can be qualitatively accounted for in terms of a potential surface dominated by pairwise, Morse-like interactions between reacting fragments. Considerable caution should be exercised in the application of Marcus-like relations to double-well potential surfaces. The relationship between h_2 and h_1 for a multiple-well potential energy surface may be considerably more complicated than the quadratic or quartic relationship observed for single-well potential surfaces in the present work. As a consequence, applications to the entire reaction coordinate of a double-well potential surface may fail, while applications to individual wells may prove more satisfactory.

I. Introduction

In the past few years, there has been a surge of interest in understanding how the barrier to a chemical reaction depends on ΔG° and in elucidating the factors which contribute to differences in the barrier for reactions with similar values of ΔG°.[1-16,18]

One approach for quantitatively treating such phenomena is the Marcus equation[2]

$$\Delta G^\ddagger = \Delta G_0^\ddagger + {}^1\!/_2\Delta G^\circ + (\Delta G^\circ)^2/16\Delta G_0^\ddagger \qquad (1)$$

which expresses the reaction barrier, $\Delta G^\ddagger$, in terms of an intrinsic barrier, $\Delta G_0^\ddagger$, and a thermodynamic term, $^1/_2\Delta G^\circ$ which raises or lowers the barrier depending on whether the reaction is endergonic or exergonic. The first two terms of Marcus' equation are exact in the limit of an energy additivity relationship[14,15a,b] between the transition states of three related reactions:

$$\text{A–B} + \text{A} \rightleftharpoons [\text{A–B–A}]^\ddagger \rightleftharpoons \text{A} + \text{B–A} \qquad (2)$$

$$\text{A–B} + \text{C} \rightleftharpoons [\text{A–B–C}]^\ddagger \rightleftharpoons \text{A} + \text{B–C} \qquad (3)$$

$$\text{C–B} + \text{C} \rightleftharpoons [\text{C–B–C}]^\ddagger \rightleftharpoons \text{C} + \text{B–C} \qquad (4)$$

The third term ($[\Delta G^\circ]^2/16\Delta G_0^\ddagger$) of Marcus' equation represents an approximate correction for nonadditivity.

The Marcus equation was originally derived for weak-overlap electron-transfer reactions where it is assumed that little or no overlap occurs between orbitals of the reacting molecules at the transition state.[2a] This assumption is thought to be realistic for certain classes of electron-transfer reactions, but it may seem inappropriate for reactions involving bond formation/bond breaking where overlap between orbitals of reacting molecules along the reaction coordinate is expected to be an important factor in determining the barrier height. Nonetheless, Marcus[2c] showed that eq 1 correlates with certain proton-transfer reactions and gives a barrier prediction[2b] very similar to that from the BEBO method[16] which was derived for atom-transfer reactions. Shortly thereafter, it was shown[5a] that eq 1 could be obtained by applying equivalent group assumptions[17] to the derivative of the energy change with respect to a perturbational parameter. Equivalent group assumptions have long been applied to *energy changes*, and *linear* free energy relationships, such as the Brønsted,[18] Hammett,[19] and

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(17) (a) The essential component of the equivalent group concept is that properties of molecules as a whole can often be obtained by adding up group contributions which are assigned to the individual fragments composing a molecule. The group contributions have been thought to be "transferable" between molecules to the extent that the neighboring environment of the fragments is constant from molecule to molecule. (b) S. W. Benson and J. Buss, *J. Chem. Phys.*, **29**, 546 (1958). See also ref 21a,b.

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Edwards[20] equations, are one result. Applying equivalent group assumptions to changes in an energy *derivative* leads to a *curved* free energy relationship (eq 1) which is based on essentially the same assumptions as the linear free energy relationships which have been in use for decades. Furthermore, there are no assumptions[5a] which limit eq 1 to specific classes of chemical reactions.

Recently, the question of how substituents perturb the barrier to a chemical reaction has been reexamined from a more fundamental point of view. Using the hemistructural relationship,[21a] a theory of nuclear substitution[21a] is being developed within a nonrelativistic, Born–Oppenheimer framework and, so far, has been carried out to first-order changes in Hartree–Fock wave functions.[21a,c,d] It has been found that equivalent group relationships for both energy and structure follow as a direct consequence of this limiting case,[21] and a general equation for expressing barrier heights or well depths of group-transfer reactions (eq 3) has been derived.[15b]

$$\Delta E^{\ddagger} = \Delta E_0^{\ddagger}[1 - g_2(\tau)] + \tfrac{1}{2}\Delta E[1 + g_1(\tau)] \qquad (5)$$

$\Delta E_0^{\ddagger}$ is analogous to Marcus' intrinsic barrier term and has a limiting value which approaches the average barrier (or well depth) of the corresponding identity reactions (eq 2 and 4). The functions g_1 and g_2 are odd and even functions of τ which can be expressed as a function of $\Delta E_0^{\ddagger}$, ΔE, or other parameters.[15b] About a dozen previous empirical equations for predicting barrier heights have been shown[15c] to be specific cases or simple extensions of eq 5 and correspond to different choices for g_1 and g_2. For example, setting $g_1 = \tau$, $g_2 = \tau^2$, and $\tau = \Delta E/(4\Delta E_0^{\ddagger})$ yields the Marcus equation (expressed in terms of ΔE rather than $\Delta G°$). The derivation of eq 5 assumes at least one stationary point separating reactants and products, but no distinction is made between a transition state or a stable intermediate. Consequently, it is significant that eq 5 gives a good description of SCF well depths of proton-bound dimers of rare-gas atoms[15b] and experimental well depths of 53 proton-bound dimers of amines, neutral hydrides, and anions,[15a,22] as well as SCF[13,15a] and experimental[11,12] barriers to S_N2 reactions at carbon. Equation 5 has also been applied to[15e,f] sigmatropic shifts, cycloadditions, and other reactions subject to orbital symmetry constraints and the degree of overlap between reacting orbitals at the transition state. These and other results,[15] as well as the theoretical derivation,[15b,d,21] show that Marcus-like equations (e.g., eq 5) are applicable to situations which extend beyond weak-overlap electron-transfer reactions and the other specific assumptions[15c] used to justify additional special cases[15c] of eq 5.

Although the Marcus equation has been shown to have broad applicability to both SCF and experimental results, it is significant to note that two reactions have been identified[15a,23] in which the experimental well depths differ appreciably from those predicted by eq 1:

$$\text{Cl–H} + {}^{-}\text{OH} \rightleftharpoons \text{Cl}^- + \text{H}_2\text{O} \qquad (6)$$

$$\text{Br–H} + {}^{-}\text{OH} \rightleftharpoons \text{Br}^- + \text{H}_2\text{O} \qquad (7)$$

The deviations from the Marcus equation are about 10 kcal and are substantial enough so that empirical alternatives[15c] to the Marcus equation lead to little improvement. The deviations are not "intrinsic" properties of $^{-}$OH, Cl$^-$, and Br$^-$ since other reactions involving these anions show reasonable agreement with Marcus' equation.[15a]

Two additional examples of deviations involving SCF potential surfaces can be found in results reported by Radom.[24] Although Radom did not actually apply the Marcus equation to his results, it is found (vide infra) that while most of his examples follow the Marcus equation, the reactions involving LiF with HFH$^+$ and HFCH$_3^+$ show marked deviations.

It should also be noted that Allen and Desmeules[25] have reported SCF well depths (4-31 G basis set) for a substantial number of proton-bound dimers of simple neutral hydrides, and most of these values exhibit significant deviations from Marcus' equation. It was implied[25] that many of these dimers are associated with double-minima potential wells, and it has also been pointed[15a] out that Marcus' equation may exhibit systematic deviations when applied to double-minima systems. It was noted [15a] that the deviations associated with the results of Allen and Desmeules[25] are consistent with double-minima wells and that other factors[15a] could also be important. An example clearly associated with a double-minima potential well is the proton-bound dimer of water and phosphine.

The Marcus equation has been extensively applied to solution-phase reactions,[2,5,8,10,11,14] and the authors are unaware of any examples of an unequivocable breakdown. In the gas phase, deviations greater than a couple of kilocalories are unusual, and agreement to within tenths of a kilocalorie is frequent.[12,13,15] Consequently, the breakdowns observed for the proton-bound dimers Cl-H-OH$^-$, Br-H-OH$^-$, LiF-H-FH$^+$, LiF-H-FCH$_3^+$, H$_3$P-H-OH$_2^+$, etc. are of considerable interest, and some of these will be examined in detail.

II. Reaction Coordinates and Potential Energy Surfaces

A. The Energy Change along the Reaction Coordinate. It has recently been demonstrated that the energy change along an arbitrary reaction coordinate can be represented by

$$E(X) = \Delta E_0^{\ddagger}(1 - h_2(X)) + \tfrac{1}{2}\Delta E(1 + h_1(X)) \qquad (8)$$

where $h_1(X)$ and $h_2(X)$ are linearly independent functions of the variable (X) describing the reaction coordinate, $\Delta E_0^{\ddagger}$ is an intrinsic barrier term analogous to that appearing in eq 1, and ΔE is the energy difference between reactants and products.[15d] It was also shown that if $h_2 = h_1^2$, then the barrier height ($\Delta E^{\ddagger} = E(X^{\ddagger})$, where $X^{\ddagger}$ is the position of the stationary point) follows the Marcus equation and that each half of the reaction coordinate function ($0 \leq X \leq X^{\ddagger}$ and $X^{\ddagger} \leq X \leq 1$) is a mirror image of the other, after making suitable scale adjustments to the horizontal and vertical axes ("scaled" symmetry relationship).[15d] The Marcus equation for the *barrier height* holds for any reaction coordinate where $h_2 = h_1^2$ (i.e., the square relationship) and is completely independent of the form of h_1 and h_2.[15d] The barrier *height* can be obtained from ΔE and $\Delta E_0^{\ddagger}$ through the Marcus equation without specific knowledge of h_2 or h_1.

The intrinsic barrier term in eq 8 is usually approximated by averaging the barriers of the two identity reactions (eq 2 and 4). Even within the first-order theory[21a] mentioned earlier, there may be nonadditive contributions[15b] to $\Delta E_0^{\ddagger}$ which constitute a second potential source of deviations from Marcus' equation. Consequently, a general treatment of the breakdown of Marcus' equation can be formulated in terms of the breakdown of the square relationship ($h_2 = h_1^2$) and the degree of nonadditivity observed in $\Delta E_0^{\ddagger}$.

B. Reaction Coordinate Variable. In principle, the reaction coordinate can be expressed in terms of Cartesian coordinates, bond order coordinates, or some other suitable variable. The actual choice is immaterial with regard to analyzing barrier heights in terms of the Marcus' equation since the essential consideration is the relationship between h_2 and h_1 and not the specific form of these functions. Nonetheless, the nature of h_1 and h_2 are of interest, since the *position* of stationary points along the reaction coordinate depends not only on the relationship between h_2 and h_1, but also on the precise form of h_1 (see section VI). Moreover, it has been found[15e,h] (vide infra) that coordinate transformations

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(26) For reaction coordinates where $\Delta E \neq 0$ or for reaction coordinates which are symmetrical with respect to reflection about $n = {}^1/_2$.

Table II. Comparison of Calculated Values of $\Delta E^{\ddagger}$ with $\Delta E^{\ddagger}_{SCF}$

	$\Delta E^{\ddagger}_{Marcus}$		$\Delta E^{\ddagger}_{quartic}$				$\Delta E_0^{\ddagger}$		
reaction	additive[a]	nonadditive[b]	pure[c]	mixed[d]	$\Delta E^{\ddagger}_{SCF}$	$\Delta E^{\ddagger}_{iden}$	additive[a]	nonadditive[b]	ΔE
HF/$^{-}$OH	−64.8	−64.4	−67.3	$\underline{-66.8}$	$\underline{-66.1}$	−62.7/−40.8	−51.8	−51.3	−24.7
HCl/$^{-}$OH	−94.4	−98.6	−108.3	$\underline{-108.5}$	$\underline{108.5}$	−31.7/−40.8	−36.3	−42.5	−89.0
H_3O^+/PH_3[e]	−31.0	−26.7	−27.0	$\underline{-20.6}$	$\underline{-28.4}$	−44.7/−13.4	−29.0	−24.8	−3.74
H_3O^+/PH_3[f] (inner)	2.8	2.6	2.8	$\underline{2.7}$	$\underline{2.7}$	2.3/0.0	1.2	0.8	2.60
HFH$^+$/LiF	−121.6	−126.5	−139.1	$\underline{-129.7}$	$\underline{-129.9}$	−42.8/−63.1	−52.9	−59.4	−109.2
CH_3F/H^-[e]	6.2	12.9	21.9	$\underline{3.9}$	$\underline{4.1}$	7.9/60.2	34.0	43.0	−77.9
CH_3F/H^-[f] (inner)	14.8	20.8	28.8	$\underline{16.8}$	$\underline{16.3}$	19.4/62.8	41.1	48.0	−65.7

[a] Calculated from the average of the identity barriers. [b] Calculated from the symmetric (intrinsic) component of the cross reaction. [c] Calculated from eq 8 by setting $h_2 = h_1^4$. [d] Calculated from eq 8 by setting $h_2 = c_2h_1^2 + c_4h_1^4$. The coefficients (c_2, c_4) are listed in Table III. [e] For double-minima surfaces, ΔE and $\Delta E_0^{\ddagger}$ are calculated on the basis of the separated reactants (AH + B and A + HB). [f] ΔE and $\Delta E_0^{\ddagger}$ are calculated on the basis of the hydrogen-bonded intermediates (AH···B), (A···HB), (AH···A), and (BH···B).

(e.g., from Cartesian coordinates to bond order coordinates) often simplify the shape of the potential energy surface and make it easier to visualize the connection between the present results and earlier work by Hughes, Ingold and Shapiro,[1a] Hammond,[1b] Thornton,[3] Kurz,[3b,c] More O'Ferrall,[4] Jencks,[7] Bruice,[6] Gajewski,[9] and others. The reaction coordinates reported in this paper have been evaluated from the minimum energy path separating reactants and products on a potential energy surface which is expressed in terms of Cartesian coordinates. It is important to note that the minimum energy path from reactants to products (i.e., the reaction coordinate) is dependent on the choice of coordinates and that the minimum energy path bears no direct relationship to the dynamics of molecules moving over a given potential surface. These points will be dealt with in more detail in subsequent papers,[15h] but since we are interested in a simple means of characterizing a potential surface, rather than carrying out dynamical calculations, the procedure described above will suffice for our present purposes. Replacing a minimum energy pathway over a Cartesian coordinate surface with a minimum energy pathway over a bond order surface is not expected to alter the general conclusions of this paper. It should also be emphasized that the energies of *stationary* points are independent of coordinates.

C. Intrinsic and Thermodynamic Components of Reaction Coordinates. In eq 8, h_2 and h_1 can be respectively represented by even and odd functions (with respect to $X = {}^1/_2$) of the reaction coordinate variable, X.[15a,d] A simple method of obtaining h_1 and h_2 is to form the sum and difference of $E(X)$ and $E(1 - X)$ from eq 8 to give

$$I(X) = \Delta E_0^{\ddagger}[1 - h_2(X)] = {}^1/_2[E(X) + E(1 - X) - \Delta E] \quad (9)$$

$$T(X) = {}^1/_2\Delta E[1 + h_1(X)] = {}^1/_2[E(X) - E(1 - X) + \Delta E] \quad (10)$$

and to solve eq 9 and 10 for $h_1(X)$ and $h_2(X)$. This allows a comparison of $h_1(X)$ and $h_2(X)$ in order to test the square relationship ($h_2 = h_1^2$) and to make a comparison of $I(X)$ of the unsymmetrical reaction (eq 3) with the average of the barrier functions for the symmetrical reactions (eq 2 and 4). In simple physical terms, the function $T(X)$ provides a measure of the extent to which ΔE propagates across the reaction coordinate[15c] and will be referred to as the *thermodynamic* function, while $I(X)$ provides a measure of the height and shape of the barrier for a hypothetical thermoneutral reaction and will be referred to as the *intrinsic* or *kinetic*[15a,b] function. Any reaction coordinate can be divided into a corresponding thermodynamic function $[T(X)]$ and intrinsic function $[I(X)]$. This separation provides a pictorial, but quantitative, means for factoring out the effect of the reaction thermodynamics on the barrier height and shape, so that reactions whose thermodynamics are different can be readily compared.

III. Results of ab Initio Calculations

The energies and structures reported in the present work have been obtained by using Gaussian 80[27] with an extended basis set (4-31 or 5-21 basis set, Table I in supplementary material). Although these basis sets have been used previously for similar problems,[13,15b,24] it should be emphasized that specific relative energies, including the energy differences between stationary points, may be in only poor to fair agreement with experiment at this level of approximation (limited basis set, no correlation correction). However, the aim of this paper is to test the relationship between calculated quantities which appear in the Marcus equation (e.g., ΔE, $\Delta E_0^{\ddagger}$, $\Delta E^{\ddagger}$) and not necessarily to compare these quantities with experimental measurements. The relationship between $\Delta E^{\ddagger}$, ΔE, and $\Delta E_0^{\ddagger}$ has been explored analytically at the Hartree–Fock limit (i.e., an infinite, complete basis set), and the general form of this relation will also hold for incomplete basis sets.[21a] This has been numerically verified from SCF calculations employing 3G and 4-31G basis sets.[15b] Consequently, even though specific calculated energies may not be in exact agreement with experimental quantities, the general relationships derived from these calculations can be expected to hold for experimental quantities.[28]

For Cl–H–OH$^-$ and F–H–OH$^-$, the optimized structures are slightly bent (Table I) but the optimized linear structures are both less than 1 kcal higher in energy than the bent structures. The intermediates of the corresponding identity reactions have a linear configuration about the bridging H nucleus. The bifurcated structures of the cross reaction intermediates are less stable compared to the nearly linear, optimized structures, so that the breakdown of the Marcus equation in the HCl/$^-$OH example cannot be attributed to the presence of a bifurcated intermediate, which was noted as one possibility.[15a] The relative energies of all three optimized configurations of Cl–H–OH$^-$ and F–H–OH$^-$ are qualitatively similar to those determined in a previous study[29] which employed a large Gaussian basis set.

The Marcus equation was applied to the reactions Cl–H + $^-$OH, F–H + $^-$OH by using the data in Table I to calculate ΔE and $\Delta E_0^{\ddagger}$ (as the average of the two identity barriers). The results are given in Table II.

IV. Evaluating Intrinsic and Thermodynamic Contributions to Reaction Coordinates—Single-Minimum Wells

A. HF/$^-$OH. 1. The Reaction Coordinate. The method for approximating the minimum energy pathway (in Cartesian coordinates) is described in Appendix I in supplementary material.

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[28] The theoretical results are in terms of ΔE and so, technically, the experimental results should be corrected for entropy effects, enthalpy corrections to 0 K, and zero-point energies. However, empirical results indicate that these effects do not result in a radical breakdown of the relationships in terms of ΔE (see ref 1c and 2–15 and others). Correlation effects are not expected to alter the relationship between $\Delta E^{\ddagger}$, $\Delta E_0^{\ddagger}$, and ΔE, although absolute magnitudes are expected to vary (J. R. Murdoch, preliminary results).

[29] H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **58**, 5627 (1973).

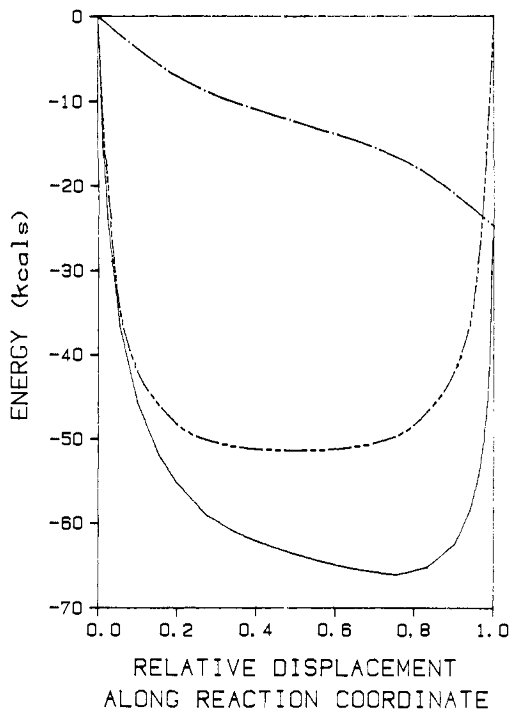

Figure 1. Energy as function of relative displacement along the reaction coordinate for the HF/$^-$OH reaction. Dashed line represents the intrinsic component and dotted–dashed line the thermodynamic component.

This pathway was then converted to bond-order coordinates[15d,h] and is illustrated in Figure 1 for F–H–OH$^-$. Application of eq 9 and 10 to the bond-order reaction-coordinate function yields the even and odd components which are illustrated by the broken lines in Figure 1. The even function provides a measure of the "intrinsic" well depth for F–H–OH$^-$ (∼−52 kcal) while the odd function indicates how the overall thermodynamics of the reaction propagates across the reaction coordinate into the stable intermediate. The effect of the thermodynamic function (i.e., the odd component) is to lower the energy of the minimum to about −66 kcal, indicating that around 14 kcal of stabilization is added to the intermediate by the overall thermodynamic change of −25 kcal. The position of the minimum is also shifted from 0.5 to 0.75 and is in the direction of the more stable side of the reaction coordinate, in accordance with the Hughes–Ingold–Shapiro postulate,[1a] Hammond's postulate,[1b] Thornton's rules,[3] the More O'Ferrall plot,[4,15e] and the Miller equation.[15d,30] Striking features of the diagram include the *absence* of any stationary points for the reactants and products, the parabolic-like appearance of the even function and the nearly linear behavior of the odd function. Such behavior is reminiscent of Kurz's demonstration[3c] that the Marcus equation can arise from the combination of a parabolic and a linear function of the reaction coordinate variable. The fact that an actual SCF reaction coordinate resembles a quadratic function if expressed in terms of bond order may be connected with the fact that the bond-order transformation is identical with the transformation used by Morse to transform an anharmonic vibrational function in Cartesian coordinates to a harmonic, quadratic vibrational function in bond-order coordinates.[31] More will be said on this topic later (section IV.D.3).

The observed deviation from the Marcus equation (−1.7 kcal) for the present SCF calculations is relatively small and is in close agreement with the deviation (−2.1 kcal) observed for the experimental numbers.[15a,23] The factors contributing to deviations from the Marcus equation can be divided into two classes: those contributing to deviations from the "square" relationship ($h_2 = h_1^2$, eq 8) and those contributing to nonadditivity in the intrinsic function, $\Delta E_0^\ddagger[1 - h_2]$.

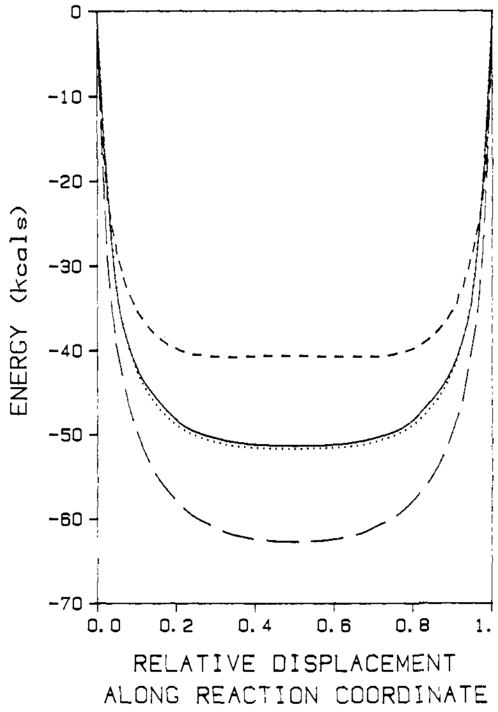

Figure 2. Comparison of intrinsic component of HF/$^-$OH reaction barrier (solid line) to barrier of the F$^-$ (large dashes) and $^-$OH (small dashes) identity reactions and to their average (dotted line).

2. Additivity of the Intrinsic Functions [$\Delta E_0^\ddagger(1 - h_2)$]. Since the two identity reactions (HO$^-$ + HOH → HOH + $^-$OH and F$^-$ + H–F → F–H + F$^-$) are thermoneutral and have no thermodynamic component, the reaction coordinate for each reaction corresponds to the respective "intrinsic" function. In Figure 2, the "intrinsic" functions of the two identity reactions have been averaged and are compared to the "intrinsic" function derived from the cross reaction according to eq 9 and 10. This average and the "intrinsic" component of the cross reaction are nearly identical over the entire range of reaction coordinate and differ by less than 0.5 kcal at the midpoint. This is particularly interesting since the two identity barriers are quite different from one another with respect to depth and overall shapes. Since the "intrinsic" functions show such a high degree of additivity, $\Delta E_0^\ddagger$ is quite close to the average of the two identity barriers.

In view of the high degree of additivity, it would be tempting to draw some conclusions about constancy of electronic structure over the fluoride and hydroxide fragments. However, previous results[21b] show that while the total energy of FHOH$^-$ is nearly additive, differing from the average of the total energies of HOHOH$^-$ and FHF$^-$ by slightly over 1 kcal (a scaled 3G basis set), the electron density distribution, and the spatial distribution of orbital and kinetic energy about each nucleus differ significantly in FHOH$^-$ from that observed in the symmetrical intermediates. Thus energy additivity does not imply the absence of interactions between O and F, but rather it depends on the mutual cancellation of interactions[21a,b] in different spatial regions. The net result is that the total energy of FHOH$^-$ is equivalent to the sum of F–H and H–OH bond energies derived from the symmetrical structures (FHF$^-$ and HOHOH$^-$), even though the spatial distribution of electron density and the spatial distribution of energy around the F, H, and OH fragments differ in the symmetrical and unsymmetrical structures.[21b] This paradox originates in part from fundamental constraints (i.e., the hemistructural relationship and virial and Hellmann–Feynman theorems) imposed on the wave function[21] and has a number of unusual consequences.[15,21]

Equation 5 is obtained[15b] for a stationary point on the A–B–C surface by adding two functions which represent separate A–B and B–C interactions derived from the identity structures (A–B–A and C–B–C). This treatment is based on first-order corrections to Hartree–Fock wave functions and does not assume fixed electronic structures for the various fragments in spite of the

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(30) A. R. Miller, *J. Am. Chem. Soc.*, **100**, 1948 (1978).
(31) P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).

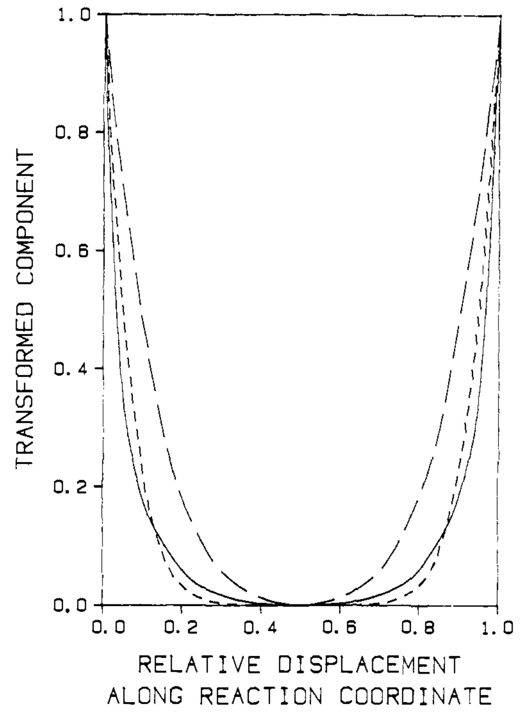

Figure 3. Comparison of h_2 (solid line) to h_1^2 (large dashes) and h_1^4 (small dashes) for HF/$^-$OH reaction.

Table III. Coefficients of Mixed Quartic Functions

	c_2	c_4
HF/$^-$OH	−0.256 227	1.206 61
HCl/$^-$OH	−0.163 055	1.120 46
H_3O^+/PH_3[a]	0.991 679	−0.235 416
H_3O^+/PH_3[b]	0.447 498	0.534 155
HFH^+/LiF	0.557 324	0.407 722
CH_3F/H^-[a]	4.326 68	−3.377 72
CH_3F/H^-[b]	0.782 339	0.105 941

[a] For the overall reaction. [b] Considering only the "inner" portion of the reaction coordinate.

apparent additivity of the A–B and B–C interactions and apparent absence of A–C interactions.[15b] At points along the reaction coordinate which lie between the transition state and the reactants or products, the structural and electronic perturbations, relative to reactants or products, should be less important than at the transition state. Consequently, the additivity of the symmetric components observed for $FHOH^-$ may be associated with the possibility that the changes in electronic structure along the reaction coordinate can be described as first-order perturbations.[21] This apparent applicability of first-order perturbation theory to many chemical problems has been noted previously[21] and is undergoing more direct tests.[21c,d]

3. The "Square" Relationship. In Figure 3, a comparison is made between the even function, h_2, for the cross reaction and the square and the fourth power of the odd function, h_1. It is noteworthy that while h_2 for the cross reaction is not identical with either h_1^2 or h_1^4, the deviation from h_1^2 at the stationary point ($X = 0.75$) is relatively small. Consequently, the Marcus equation works reasonably well for $HO^- + HF \rightarrow HOH + {}^-F$, since the square relationship ($h_2 = h_1^2$) is approximately valid at the energy minimum, and $\Delta E_0^{\ddagger}$ can be obtained to good approximation by averaging the well depths of the two symmetrical reactions ($HO^- + HOH \rightarrow HOH + {}^-OH$ and $F^- + HF \rightarrow FH + F^-$).

While the even function is not exactly the square of h_1 or the fourth power of h_1, it is found that a combination of h_1^2 and h_1^4 gives h_2 to an excellent approximation, and the quadratic and quartic coefficients are given in Table III. With this approximation for h_2, eq 8 can be used to calculate the position of the stationary point along the reaction coordinate (Table IV) and to obtain the well depth for the reaction $HO^- + HF \rightarrow HOH + {}^-F$ (Table II). Using the mixed quartic in eq 8 and applying the nonadditivity correction for $\Delta E_0^{\ddagger}$ reduces the deviation to 0.69 kcal. The value for $X^{\ddagger}$ calculated from the mixed quartic ($X^{\ddagger} = 0.73$) is also in good agreement with the SCF value ($X^{\ddagger} = 0.75$, Table IV). The main point is that the reaction coordinate can be expanded with quadratic and quartic terms in h_1, with little contribution from higher order terms. This is a significant observation and suggests that the perturbation from reactants to products is a first- or low-order perturbation in wave function,[21] but further work will be necessary to establish this point.[15f-i,21c,d]

Table IV. Comparison of Calculated Values of $X^{\ddagger}$ to $X^{\ddagger}_{SCF}$

		$X^{\ddagger}_{quartic}$			
	$X^{\ddagger}_{Marcus}$	pure	mixed	$X^{\ddagger}_{Miller}$	$X^{\ddagger}_{SCF}$
HF/$^-$OH	0.56	0.70	0.73	0.61	0.75
HCl/$^-$OH	0.76	0.82	0.83	0.85	0.90
H_3O^+/PH_3	0.92	0.88	0.89	0.95	0.79
HFH^+/LiF	0.73	0.81	0.78	0.86	0.92
CH_3F/H^-	0.33	0.22	0.30	0.17	0.45
σ	0.18	0.14	0.12	0.18	

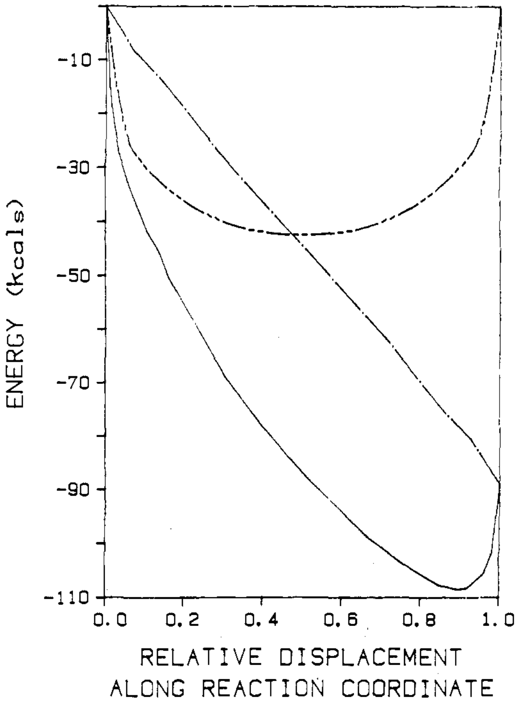

Figure 4. Energy as a function of relative displacement along the reaction coordinate for the HCl/$^-$OH reaction. Dashed line represents the intrinsic component and dotted–dashed line represents the thermodynamic component.

B. HCl/$^-$OH. The approach outlined above for HF/$^-$OH has also been applied to HCl/$^-$OH. The reaction coordinate for the unsymmetrical reaction is illustrated in Figure 4 and is qualitatively similar to that seen for HF/$^-$OH, except that the HCl/$^-$OH reaction is considerably more exothermic and the minimum is shifted farther toward product.

1. *Additivity of the Intrinsic Components* ($\Delta E_0^{\ddagger}[1 - h_2]$). When the "intrinsic" component of the cross reaction ($\Delta E_0^{\ddagger}[1 - h_2]$) is compared to the average of the identity reaction coordinates ($HO\text{–}H\text{–}OH^-$ and $Cl\text{–}H\text{–}Cl^-$), it is seen (Figure 5) that the "intrinsic" component shows substantial deviations from the average of the identity barriers over most of the reaction coordinate. At the midpoint, the deviation is over 6 kcal and the minimum value of the "intrinsic" component is actually lower than the deepest of the identity wells by 1.7 kcal. Consequently, the deviation from the Marcus equation is due, in part, to the nonadditivity of the "intrinsic" barrier. When $\Delta E_0^{\ddagger}$ is equated to the midpoint value of the intrinsic component for the unsymmetrical reaction ($HO^- + HCl \rightarrow HOH + {}^-Cl$), the prediction of the well

Table V.[a] Values of $\Delta E^{\ddagger}$ Predicted by Marcus Equation for XFH^+/FX' Reactions

	$\Delta E^{\ddagger}_{\text{iden}}$	$\Delta E_0^{\ddagger\,b}$	ΔE	$\Delta E^{\ddagger\,c}_{\text{Marcus}}$	$\Delta E^{\ddagger}_{\text{obsd}}$	$\Delta\Delta E^{\ddagger\,d}$
FF LiF	−10.88 −63.05	−36.97	−159.71	−159.95	−161.32	−1.37
FF CH_3F	−10.88 −39.62	−25.25	−80.92	−81.92	−83.90	−1.98
HF LiF	−42.75 −63.05	−52.90	−109.16	−121.56	−129.92	−8.36
CH_3F LiF	−39.62 −63.05	−51.34	−78.79	−98.29	−104.08	−5.79
FF HF	−10.88 −42.75	−26.82	−50.55	−58.05	−57.35	0.70
HF CH_3F	−42.75 −39.62	−41.19	−30.37	−57.77	−59.85	−2.08

[a] The reaction considered is the transfer of a proton from the protonated form of the first species to the second. All values in kcal/mol. [b] Calculated from the average of the identity barriers. [c] From eq 12. [d] $\Delta\Delta E^{\ddagger} = \Delta E^{\ddagger}_{\text{obsd}} - \Delta E^{\ddagger}_{\text{Marcus}}$.

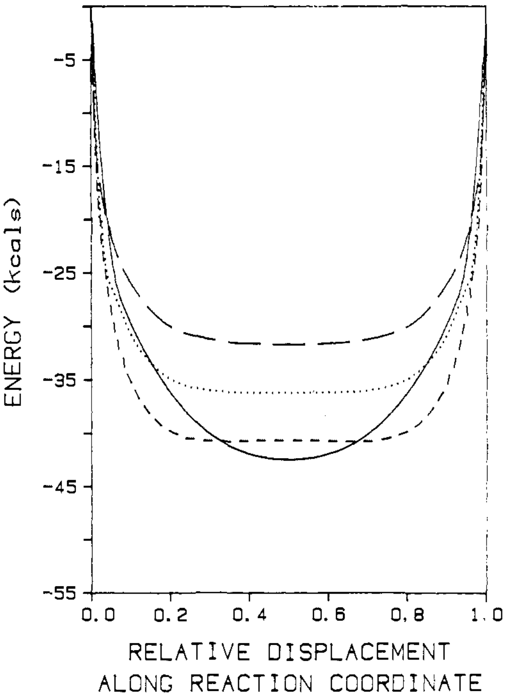

Figure 5. Comparison of intrinsic component of $HCl/^-OH$ reaction barrier (solid line) to barrier of the Cl^- (large dashes) and ^-OH (small dashes) identity reactions and to their average (dotted line).

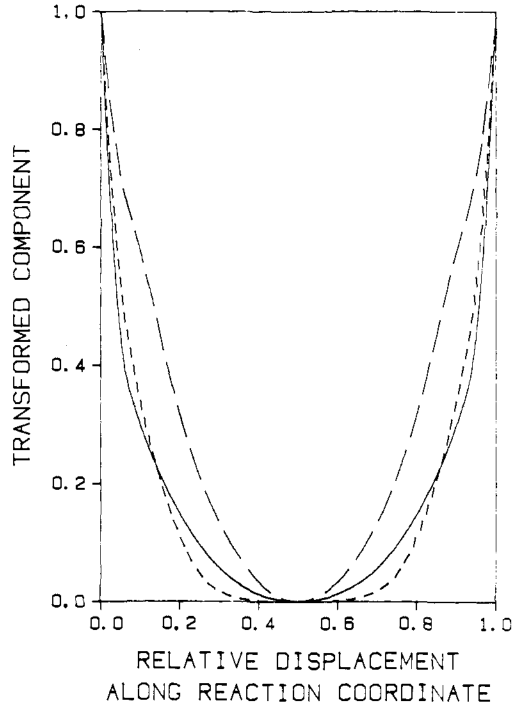

Figure 6. Comparison of h_2 (solid line) to h_1^2 (large dashes) and h_1^4 (small dashes) for $HCl/^-OH$ reaction.

depth by the Marcus equation improves by over 4 kcal (Table II).

2. The "Square" Relationship. For $HCl/^-OH$, h_2 resembles h_1^4 more closely than h_1^2 (Figure 6), and in the region near the stationary point, there is a substantial discrepancy between h_2 and h_1^2. Consequently, replacing $h_2 = h_1^2$ with $h_2 = h_1^4$ reduces the discrepancy to less than 0.2 kcal and replacing $h_2 = h_1^2$ with $h_2 = c_2h_1^2 + c_4h_1^4$ brings the error down to 0.03 kcal (Table II). The barrier position given by the mixed quartic is $X^{\ddagger} = 0.83$ compared to $X^{\ddagger} = 0.90$ from the SCF calculation (Table IV).

C. HFH^+/LiF. Pross and Radom[24] have performed Hartree–Fock calculations at the 4-31 G level in order to optimize the structures and energies of the reactants, the products, and the stable intermediates for a series of reactions of the type

$$XF\text{-}H^+ + FX' \rightarrow XF + {}^+H\text{-}FX' \qquad (11)$$

and the corresponding identity reactions. The results of applying the Marcus equation to their data are summarized in Table V. In all but two cases, reasonable agreement with the Marcus equation occurs (+0.70 to −2.08 kcal). The two exceptions are HFH^+/FLi and CH_3FH^+/FLi where the deviations are −8.36 and −5.79 kcal, respectively.

With the same general procedure as described above and in Appendix I, we have calculated the reaction coordinate (Figure 7) for the reaction $HFH^+ + FLi \rightarrow HF + HFLi^+$, which also happens to give the largest deviation from the Marcus equation. The deviations from the Marcus equation follow the same general pattern observed for the $HCl/^-OH$ case. The "intrinsic" function for the cross reaction is nonadditive by over 6 kcal (Figure 8), and the deviations due to a breakdown of the square relationship are significant (Figure 9, Table II). Correcting for nonadditivity and using $h_2 = c_2h_1^2 + c_4h_1^4$ gives agreement with the observed well depth to within 0.2 kcal (Table II). The barrier position given by the mixed quartic ($X^{\ddagger} = 0.78$) is in fair agreement with that from the SCF calculation ($X^{\ddagger} = 0.92$, Table IV).

D. Breakdown of the Marcus Equation for Single-Stationary-Point Reaction Coordinates. 1. The Marcus Equation and Nonadditive Substituent Effects. It has been demonstrated that the first two terms of the Marcus equation

$$\Delta E^{\ddagger} = \Delta E_0^{\ddagger} + \tfrac{1}{2}\Delta E + \Delta E^2/16\Delta E_0^{\ddagger} \qquad (12)$$

are exact in the limit of an additivity relationship between the three transition states for the identity and cross reactions (eq 2–4).[14,15a,b] This additivity relationship also requires that $\Delta E_0^{\ddagger} = \frac{1}{2}(\Delta E_{AA}^{\ddagger} + \Delta E_{CC}^{\ddagger})$, where $\Delta E_{AA}^{\ddagger}$ and $\Delta E_{CC}^{\ddagger}$ are the barriers of the two identity reactions (eq 2 and 4). The $\Delta E^2/16\Delta E_0^{\ddagger}$ term arises from the "square" relationship between h_2 and h_1 in eq 8 and represents an approximate correction for nonadditivity. Consequently, the success of the Marcus equation will be tied to the degree to which it describes nonadditive substituent effects. Deviations from additivity in the intrinsic barriers and departure

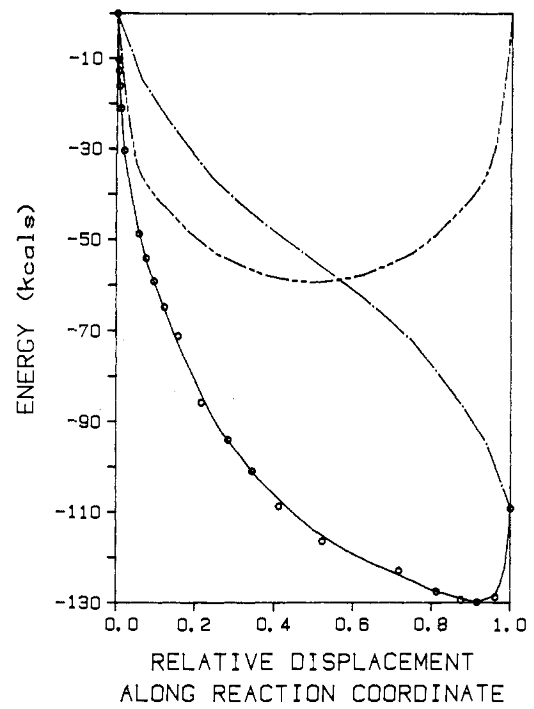

Figure 7. Energy as a function of relative displacement along the reaction coordinate for the HFH^+/LiF reaction. Circles represent the actual calculated points, and the solid line represents an approximation of the reaction coordinate derived from the data points. Dashed line represents the intrinsic component of the function represented by the solid line, and the dotted-dashed line represents the thermodynamic component.

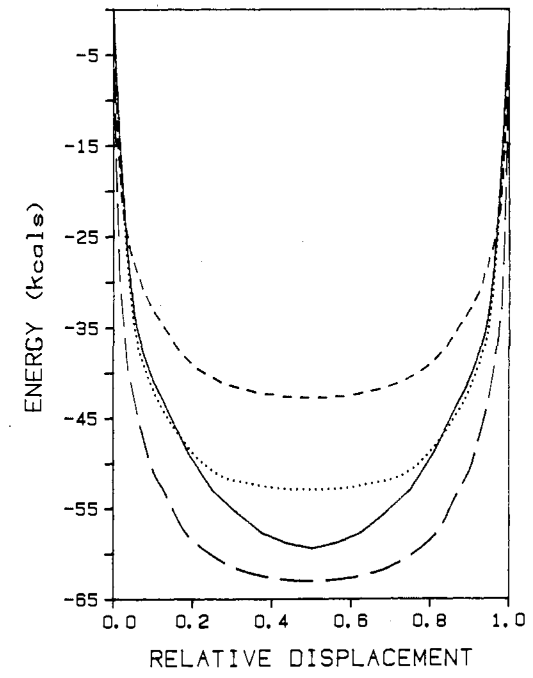

Figure 8. Comparison of intrinsic component of HFH^+/LiF reaction barrier (solid line) to barrier of the LiF (large dashes) and HF (small dashes) identity reactions and to their average (dotted line).

from the “square” relationship ($h_2 = h_1^2$) will result in nonadditive contributions which the Marcus equation cannot give an adequate account. In the large majority of cases examined so far,[12,13,15,24] these problems appear to be minimal and seldom produce errors exceeding 2 kcal. Deviations from the “square” relationship do not appear significant for reactions with stationary points near 0.5 or near the extremes of the reaction coordinate (0.0 or 1.0). Nonadditive intrinsic barriers, judging from the $HF/^-OH$ case and previous samples,[12,15,24] are apparently unusual. The examples

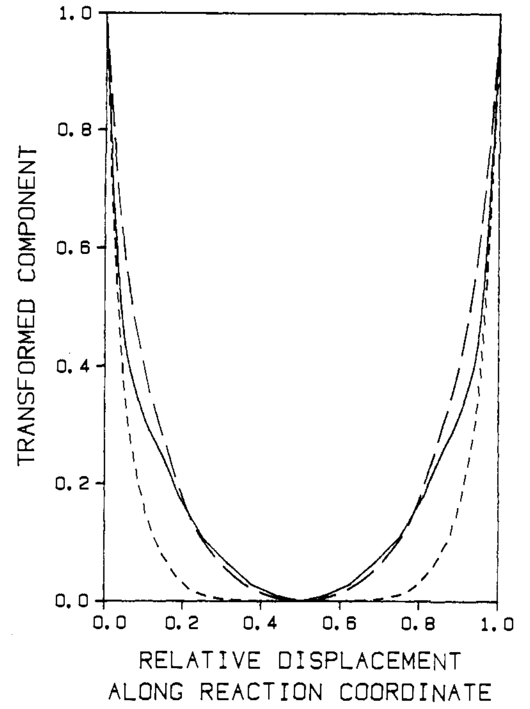

Figure 9. Comparison of h_2 (solid line) to h_1^2 (large dashes) and h_1^4 (small dashes) for HFH^+/LiF reaction.

of nonadditive intrinsic barriers are associated with values of $|\Delta E|$ substantially larger than $|\Delta E_0^\ddagger|$ (Table V), although it should be pointed out that this is not a sufficient condition for nonadditive $\Delta E_0^\ddagger$.[15b] Furthermore, the fact that $|\Delta E| < |\Delta E_0^\ddagger|$ does not necessarily guarantee that $\Delta E_0^\ddagger$ will be additive,[15b] although breakdowns of intrinsic barrier additivity which are comparable to those seen for $HCl/^-OH$ or HFH^+/FLi have not yet been observed for reactions where $\Delta E \approx 0$ or $|\Delta E| << |\Delta E_0^\ddagger|$.

2. General Nonadditivity Relationships. Pauling[32] has noticed that deviations from bond energy additivity can often be represented as the square of the difference of two properties characteristic of each of the bonded fragments. For example, the energy (D_{AB}) required to dissociate A–B to A· + ·B is given by

$$D_{AB} = \tfrac{1}{2}(D_{AA} + D_{BB}) - (\chi_A - \chi_B)^2 \qquad (13)$$

where D_{AA} and D_{BB} are the A–A and B–B dissociation energies respectively, and χ_A and χ_B are parameters characteristic of the A and B fragments. Pauling recognized that χ_A and χ_B correlate with the ability of the A and B fragments to attract electron density and used these parameters to define fragment or atomic electronegativities. Pauling's finding that the deviations from additivity can be represented by parameters characteristic of each fragment is a significant one and suggests that deviations from additivity in other situations (e.g., nonadditive intrinsic barriers) might be treated in an analogous manner.

This speculation has some support from previous work[21a] where a theory of nuclear substitution was applied to energy changes along the sequence A–A, A–B, B–B where A and B are arbitrary fragments. By combining the virial theorem and the equation describing the changes in kinetic energy after successive perturbations (eq 17, ref 21a), it is possible to show[15i] that the deviation (Δ) from additivity for the A–B bond energy[28] is given by

$$\Delta = \delta\mathbf{P}\cdot\delta\mathbf{P} \qquad (14)$$

where $\delta\mathbf{P}$ is a vector whose elements are related to changes in MO coefficients which occur after switching an A fragment with a B fragment (i.e., A–A + B–B → A–B + B–A). A detailed discussion of this finding will be given elsewhere,[15i] but it is sufficient to note that Pauling's relationship (eq 13) has a nonadditivity correction which is a special case of eq 14 and corre-

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[32] L. Pauling, “The Nature of the Chemical Bond”; Cornell University Press; Ithaca, NY, 1960.

sponds to a *one*-component vector.

Equation 14 is a general relationship[33] and is exact within the limit of first-order corrections to Hartree–Fock wave functions.[21a] This suggests that empirical application of eq 14 to the problem of nonadditive intrinsic barriers may be fruitful and suggests that intrinsic barrier nonadditivity for group-transfer reactions may be related to differences in quantities such as electronegativity, polarizability, ionization potential,[34a] electron affinity,[34a] proton affinity,[34b] bond dissociation energy,[34c] methyl cation affinity,[34d] and/or hydride affinity[34e] and so forth.[34f] Even though substantial departures from intrinsic barrier additivity appear to be the exception, the question of nonadditivity is an important one and will be dealt with quantitatively elsewhere.

3. The Significance of the Square Relationship. The "square" relationship has a physically interesting origin in that it follows from a two-term expansion of the reaction coordinate in terms of suitable functions. For example, the two-term Fourier expansion of a reaction coordinate, common in twofold rotational barrier problems,[35]

$$V(\phi) = \tfrac{1}{2}V_1(1 - \cos\phi) + \tfrac{1}{2}V_2(1 - \cos 2\phi) \qquad (15)$$

corresponds to $V_1 = \Delta E$, $V_2 = \Delta E_0^\ddagger$, $h_2 = \cos^2\phi$, and $h_1 = -\cos\phi$ and follows the Marcus equation exactly.[15g]

It is rather interesting that h_1 and h_2 for the well-depth problems considered in Table II are low-order polynomials in bond order. The fact that h_1 is nearly linear in bond order and that h_2 is largely accounted for by quadratic and quartic terms in h_1 is particularly intriguing. Empirically, this can be understood by noting that the Morse equation[31] is quadratic in bond order

$$E = D_e(1 - n_{AB})^2 - D_e \qquad (16)$$

$$n_{AB} = e^{-a(r-r_0)} \qquad (17)$$

where E is the bond energy of A–B at distance r, D_e is the A–B bond dissociation energy, n_{AB} is defined as the bond order between A–B,[36] r_0 is the A–B bond distance at the energy minimum, and "a" is a constant. If a two-dimensional potential surface for linear A–B–C is constructed by summing pairwise interactions between A–B, B–C, and A–C where the pairwise interactions are represented by Morse-like functions, it can be seen from eq 16 and 17 that the A–B and B–C interactions will provide up to quadratic terms in bond order. The A–C distance is the sum of the A–B and B–C distances (for linear A–B–C), and it can be shown[15h] that the A–C bond order is related to the *product* of the B–C and A–B bond orders. Along the reaction coordinate, this product term is approximately of the form $(1 - n)n$ (where n is the bond order between B–C), so that the A–C bond-order expression will lead to quartic terms in "n" after substitution into eq 16.[37] The application of this pairwise, Morse-like potential surface to certain atom-transfer reactions (e.g., F· + H–H → F–H + ·H) has been examined.[15h] The surface for the cross reaction has been determined from the bond dissociation energies of F–H and H–H and the surfaces for the two associated identity reactions (F–H + ·F → ... and H–H + ·H → ...).[15h] The empirical surface gives a good account of an ab initio potential surface (i.e., the barrier height, the "intrinsic" and "thermodynamic" functions (f_2 and f_1), and the potential energy surface in the vicinity of the reaction coordinate).[15h] This and other applications will be reported elsewhere,[15h] but the results suggest that pairwise, Morse-like interactions can account for the quadratic and quartic terms observed in h_2, the breakdown of the "square" relationship leading to the Marcus equation, and the nearly linear behavior observed for h_1 as a function of bond order.[15h] In more fundamental terms, the observation that these potential energy surfaces can apparently be described in terms of pairwise interactions may be linked to the degree to which the perturbation from reactants to products can be described as a first-order perturbation in wave function.[21]

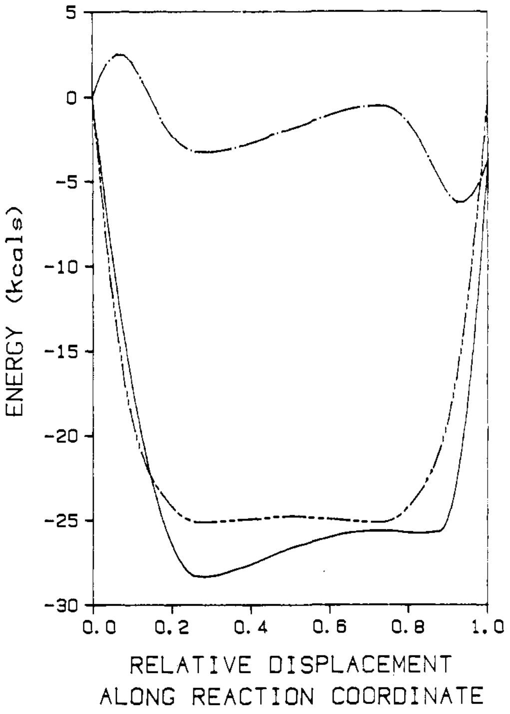

Figure 10. Energy as a function of relative displacement along the reaction coordinate for the H_3O^+/PH_3 reaction. Dashed line represents the intrinsic component and dotted–dashed line represents the thermodynamic component.

V. Evaluating Intrinsic and Thermodynamic Contributions to Reaction Coordinates—Double-Minimum Wells

A. Proton-Bound Dimers ($H_2O{\cdot}H{\cdot}PH_3^+$). The proton-bound dimer of water and phosphine ($H_2O{\cdot}H{\cdot}PH_3^+$) is an example of a system exhibiting a double well,[25] and the reaction coordinate is illustrated in Figure 10. Note that the thermodynamic function departs markedly from linearity and that the lower energy minimum lies toward the less stable side of the reaction coordinate. This latter feature is in contrast to the behavior observed by Wolfe[13] in a study of S_N2 reaction coordinates. Wolfe's systems exhibit double minima, but in all cases the lower energy minimum lies toward the more stable side of the reaction coordinate. Wolfe used this observation as an assumption in deriving an "extended" Marcus-like equation, and the present results indicate that Wolfe's equation should be used with caution.

The reaction coordinate for the $H_2O{\cdot}H{\cdot}OH_2^+$ reaction has not yet been completely optimized except at the midpoint of the reaction coordinate (Table I). The average energy of the two respective midpoints on the reaction coordinates for the symmetrical reactions ($H_3O^+ + H_2O$ → ... and $PH_4^+ + PH_3$ → ...) is 4.2 kcal lower than the midpoint of the "intrinsic" component of the cross reaction barrier, indicating substantial nonadditivity in the intrinsic barrier.

The comparison of h_2 with h_1^2 and h_1^4 is particularly instructive (Figure 11) since h_2 bears virtually no resemblance to either h_1^2 or h_1^4 except near $X = 0.2$, 0.5, and 0.8. However, the Marcus equation, formally applied to the entire reaction coordinate, is consistent with having a stationary point located at $X = 0.52$ where h_2 is very close to h_1^2, and it gives an accurate prediction of the energy at this displacement (using the nonadditive $\Delta E_0^\ddagger$). Because of the flatness of the well (Figure 10), this energy is close to $\Delta E^\ddagger$, and the Marcus equation appears to "work" (to within 2 kcal,

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[33] An equation similar to eq 14 can be derived along similar lines and is the general form of the multiparameter free energy relationships such as the Edwards equation.[20] This relationship will be developed in ref 15i.

[34] (a) For electron transfer. (b) For proton transfer. (c) For atom transfer. (d) For methyl transfer. (e) For hydride transfer. (f) Extensions to other group-transfer reactions should be obvious.

[35] L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 2371 (1972).

[36] Pauling's definition of bond order sets the constant "a" to 1/0.26.[32] Equation 17 leaves "a" as an adjustable constant.

[37] If bond order conservation is strictly followed along the reaction coordinate, the form of the product term is $(1 - n)n$. In other cases, the "1" is replaced by a function of n whose deviation from unity depends on the degree of departure from bond order conservation. For many empirical surfaces, deviations from bond-order conservation are small (e.g., ref 15h).

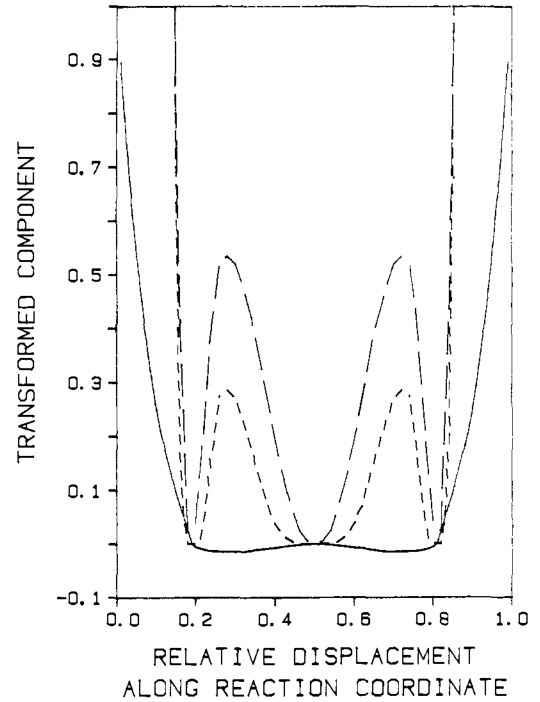

Figure 11. Comparison of h_2 (solid line) to h_1^2 (large dashes) and h_1^4 (small dashes) for the overall H_3O^+/PH_3 reaction coordinate.

Table II). Similar results are seen when h_2 is set equal to h_1^4, but the mixed quartic yields a deviation of almost 8 kcal. This is because the mixed quartic gives a poor representation of h_2 which is flat between $0.2 \leq X \leq 0.8$, while h_1^2, h_1^4, and the mixed quartic all show large oscillations across this region. The results indicate that the Marcus equation can give reasonable predictions of well depths for double-minima situations but that this success may be due to fortuitous circumstances which will not necessarily be general.

The markedly nonlinear appearance of h_1 (Figure 10) and the poor agreement between h_2 and either h_1^2 or h_1^4 (Figure 11) suggest that the "square" relationship holds best when the reaction coordinate can be expressed as a low-order expansion in terms of some suitable variable (e.g., bond order). Apparently, the "square" relationship is most reliable when h_1 does not contain appreciable nonlinear contributions which suggests that the Marcus equation depends on the extent to which the potential surface (at least along the reaction coordinate) can be described as a low-order perturbation. The present results indicate that this condition apparently applies to many potential surfaces (e.g., $FH + {}^-OH \rightarrow F^- + HOH$), but the $H_3O^+ + PH_3$ reaction shows that even if this is the case for certain potential energy surfaces, it is unlikely to apply in all cases. Nonetheless, the first-order condition may hold for portions of the potential surface, and consequently, one way of dealing with double minima is to limit consideration to the part of the reaction coordinate which lies between the two minima. The Marcus equation can be applied to the double-minima situation where one minimum corresponds to the "reactants", the other to the "products", and the maximum between them to the "transition state".[12,13]

Figure 12 depicts the barrier and the intrinsic and thermodynamic components for the portion of the reaction coordinate between the two intermediates. The intrinsic function is slightly nonadditive (−0.4 kcal), and Figure 13 shows that h_2 is similar to both h_1^2 and h_1^4. Consequently, it is not surprising that the Marcus equation is in error by only 0.1 kcal (Table II). The near additivity of the symmetric functions and the simplification of the thermodynamic function to the nearly linear sigmoid shape lend some support to the earlier speculation that limiting the range of the potential surface might improve the degree to which first-order perturbation theory is an adequate description. Considering the flatness of the reaction coordinate near the transition state, the barrier position predicted by the mixed quartic function ($X^\ddagger = 0.89$) is in reasonable agreement with the SCF value ($X^\ddagger = 0.79$, Table IV).

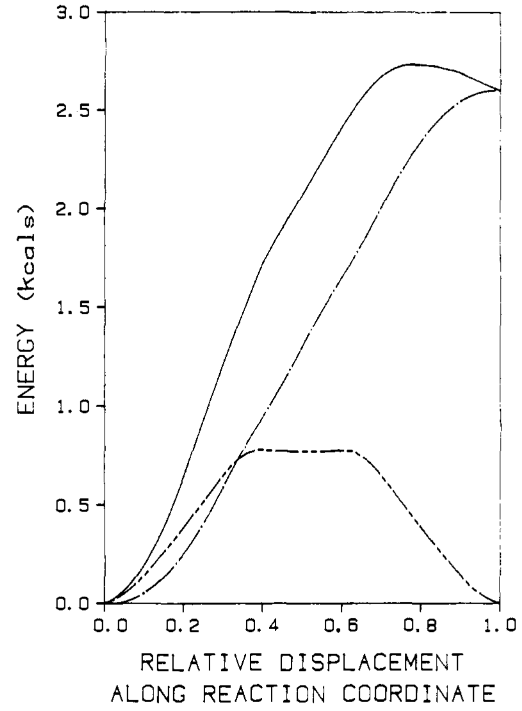

Figure 12. Energy as a function of relative displacement along the reaction coordinate for the "inner" portion of the H_3O^+/PH_3 reaction coordinate. Dashed line represents the intrinsic component and dotted-dashed line represents the thermodynamic component.

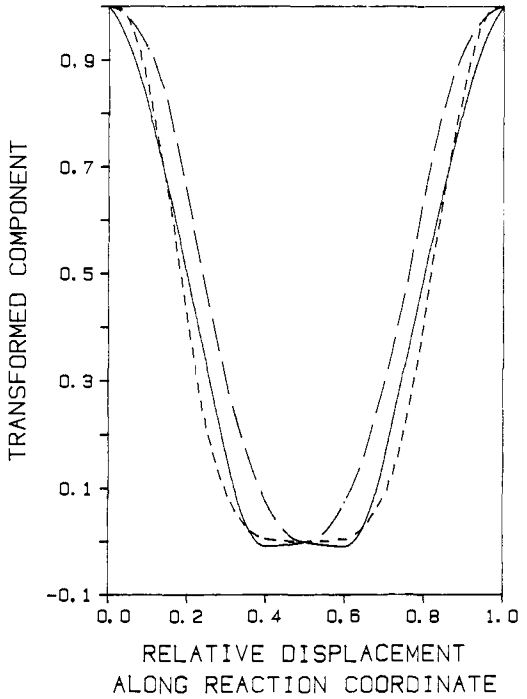

Figure 13. Comparison of h_2 (solid line) to h_1^2 (large dashes) and h_1^4 (small dashes) for the "inner" portion of the H_3O^+/PH_3 reaction coordinate.

B. Nucleophilic Substitution ($H^- + CH_3F \rightarrow H{-}CH_3 + F^-$). Gas-phase S_N2 reactions are generally thought to proceed through double-minima reaction coordinates, and this is supported by both experimental[12] and theoretical work.[13,38] Dedieu and Veillard[38] have studied the reaction

$$H^- + CH_3F \rightarrow H{-}CH_3 + F^- \qquad (18)$$

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[38] A. Dedieu and A. Veillard, *J. Am. Chem. Soc.*, 94, 6730 (1972).

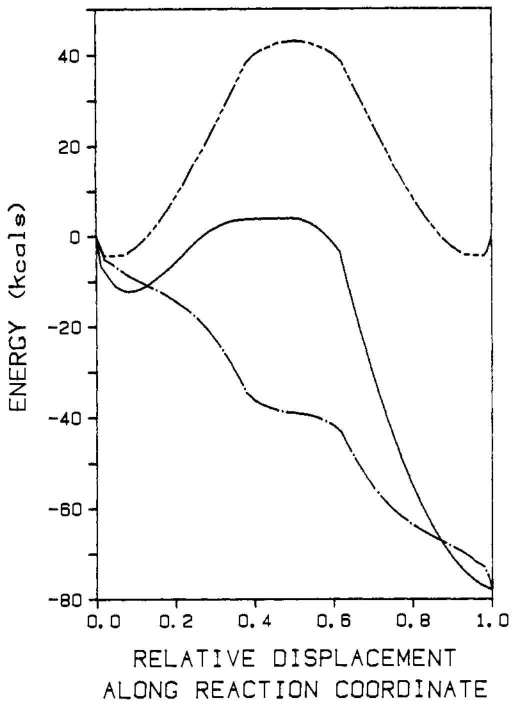

Figure 14. Energy as a function of relative displacement along the reaction coordinate for the CH_3F/H^- reaction. Dashed line represents the intrinsic component and dotted–dashed line the thermodynamic component.

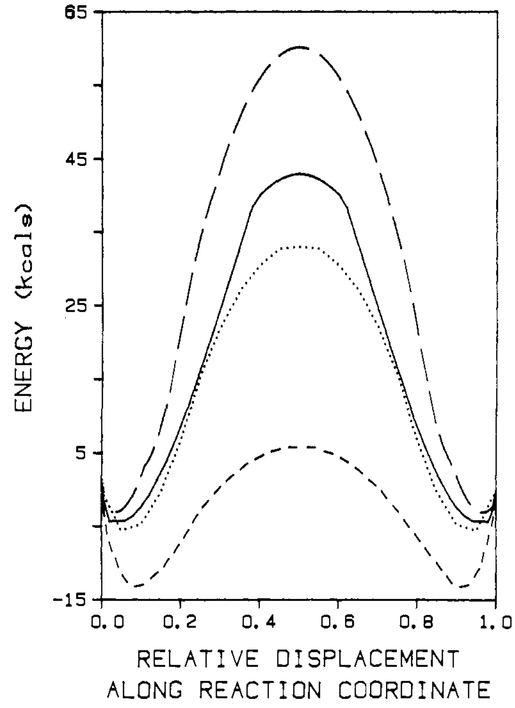

Figure 15. Comparison of intrinsic component of CH_3F/H^- reaction barrier (solid line) to barrier of the CH_4 (large dashes) and CH_3F identity reactions (small dashes) and to their average (dotted line).

using a large Gaussian basis set with partial geometry optimization and configuration interaction.

When the Marcus equation is applied to the overall reaction (Figure 14) and $\Delta E_0^\ddagger$ is calculated by averaging the identity reaction barriers, the barrier of the cross reaction is overestimated by 2.1 kcal (see Table II). Figure 15 shows that the symmetric functions are nonadditive by almost 10 kcal, and it is found that h_2 differs substantially from both h_1^2 and h_1^4. With the nonadditive value for $\Delta E_0^\ddagger$, a larger deviation (8.8 kcal) from the Marcus equation is observed, and the deviation from the pure quartic equation is even greater (17.8 kcal). Thus, the agreement with the Marcus equation which is observed when $\Delta E_0^\ddagger$ is equated to the average of the identity reaction barriers is not due to additivity of the intrinsic barriers or to satisfaction of the square relationship between h_2 and h_1. Rather, the intrinsic functions are nonadditive and h_2 differs substantially from h_1^2, and these two effects are cancelling one another. When the nonadditive value for $\Delta E_0^\ddagger$ is used in conjunction with the mixed quartic equation, the observed deviation is only 0.2 kcal (Table II).

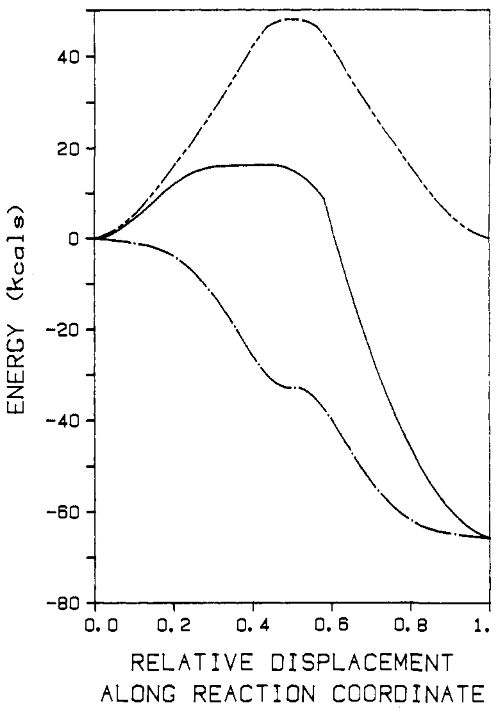

Figure 16. Energy as a function of relative displacement along the reaction coordinate for the "inner" portion of the CH_3F/H^- reaction coordinate. Dashed line represents the intrinsic component and dotted–dashed line the thermodynamic component.

The reaction coordinates of reaction 18 and the corresponding identity reactions all exhibit minima between the reactants and the transition states. This system has, therefore, been treated in an analogous fashion to the treatment of the double minimum for the H_3O^+/PH_3 system by considering only the portion of the reaction coordinate between the transition state and the minima on either side (Figures 16–18).

For this "inner" portion of the reaction coordinate, the Marcus equation underestimates the barrier height by a little less than 1.5 kcal when $\Delta E_0^\ddagger$ is estimated from the average of the identity barriers. However, the intrinsic functions are nonadditive, and the deviation from the Marcus equation obtained when the nonadditivity is taken into account actually increases (4.5 kcal). An even larger deviation (12.5 kcal) from the pure quartic equation is observed. Again, for this portion of the reaction coordinate, the Marcus equation accurately predicts $\Delta E^\ddagger$ when the additive value for $\Delta E_0^\ddagger$ is used only because the nonadditivity of the intrinsic functions and the deviation from the square relationship cancel one another. When the intrinsic barrier nonadditivity and the deviations from the square relationship are both taken into account, the predicted value of $\Delta E^\ddagger$ agrees with the SCF value to within 0.5 kcal (Table II).

VI. Relative Displacements of the Stationary Points

The derivation of the Marcus equation and other similar equations from the equation which describes the barrier (eq 8) involves determining the displacement of the stationary point by differentiating the barrier equation (eq 8) and setting the derivative equal to zero. The location of this stationary point is then substituted into the barrier equation, yielding an equation for the energy at the stationary point. If the relationship between h_2 and h_1 which is being used does not adequately describe the entire reaction coordinate, the resulting equation for $\Delta E^\ddagger$ may break

Table VI. Comparison of Calculated Values of $X^{\ddagger}$ and $1 - X^{\ddagger}$ to Observed Bond Orders

	$X^{\ddagger}_{\text{Marcus}}$	$X^{\ddagger}_{\text{Miller}}$	$n^{\ddagger}_{\text{obsd}}$	$1 - X^{\ddagger}_{\text{Marcus}}$	$1 - X^{\ddagger}_{\text{Miller}}$	$1 - n^{\ddagger}_{\text{obsd}}$
FFH^+/FLi	1.04	0.99	1.00	...	0.01	0.02
FFH^+/FCH_3	0.90	0.97	0.97	0.10	0.03	0.05
CH_3FH^+/FLi	0.69	0.80	0.89	0.31	0.20	0.16
FFH^+/FH	0.76	0.89	0.87	0.24	0.11	0.17
HFH^+/FCH_3	0.59	0.67	0.76	0.41	0.33	0.25
HFH^+/FLi	0.76	0.86	0.93	0.24	0.14	0.11
σ	0.17	0.07		0.13	0.05	

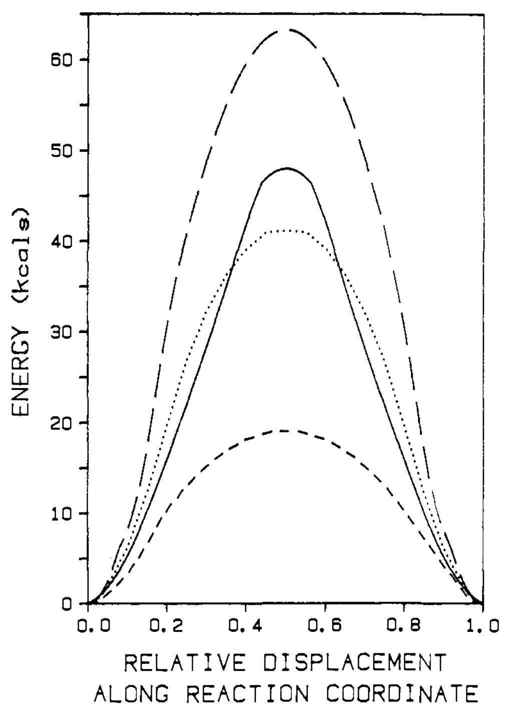

Figure 17. Comparison of intrinsic component of the "inner" portion of the CH_3F/H^- reaction barrier (solid line) to the corresponding barrier of the CH_4 (large dashes) and CH_3F (small dashes) identity reactions and to their average (dotted line).

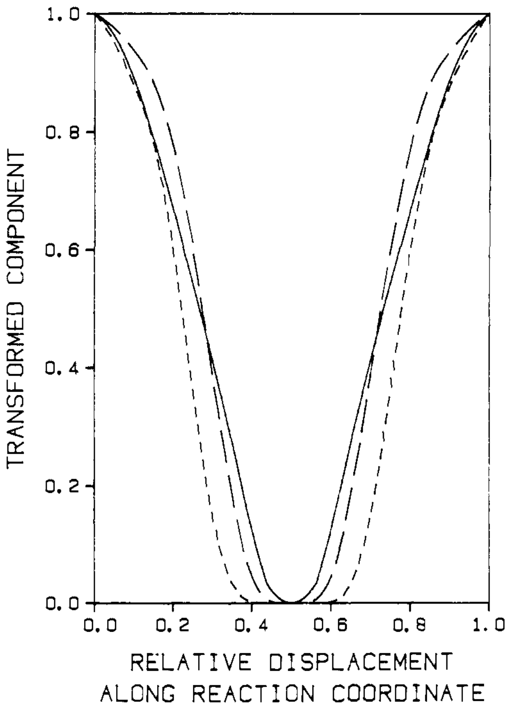

Figure 18. Comparison of h_2 (solid line) to h_1^2 (large dashes) and h_1^4 (small dashes) for the "inner" portion of the CH_3F/H^- reaction coordinate.

down, even if the h_2/h_1 relationship holds at the stationary point, because the stationary point may be located at a displacement different from that obtained from the differentiation.

It can be shown[15d] that when $h_2 = h_1^2$ (which leads to the Marcus equation) the equation for the displacement of the stationary point, $X^{\ddagger}$, is

$$\tfrac{1}{2}[1 + h_1(X^{\ddagger})] = \tfrac{1}{2} + \Delta E/8\Delta E_0^{\ddagger} \qquad (19)$$

Similarly, when the quartic relationship $h_2 = h_1^4$ is satisfied

$$\tfrac{1}{2}[1 + h_1(X^{\ddagger})] = \tfrac{1}{2} + \tfrac{1}{4}(\Delta E/\Delta E_0^{\ddagger})^{1/3} \qquad (20)$$

Equation 19 and 20 give the value of h_1 at the stationary point, $X^{\ddagger}$, and in order to find $X^{\ddagger}$, it is necessary to know the form of the function, h_1. However, Figures 1, 4, 7, 12, and 16 illustrate that h_1 is a fairly linear function of X when X is expressed in terms of bond order coordinates, and consequently, one could estimate the position of the stationary points by using eq 19 and 20 and the approximation, $^1/_2[1 + h_1(X)] = X$.[3c]

Table VI lists the observed $X^{\ddagger}$ for all of the systems considered in the previous section, along with the values obtained by substituting the nonadditive value of $\Delta E_0^{\ddagger}$ into eq 19 and 20, as well as the values obtained from the mixed quartic barrier functions described in the previous section. A simple relationship for predicting the barrier position has recently been proposed by Miller:[15d,30]

$$X^{\ddagger} = 1/(2 - \Delta E/\Delta E^{\ddagger}) \qquad (21)$$

and the results of applying this relationship are also included in Table VI, along with the standard deviations for each method.

The Marcus and Miller[15d,30] models can also be used to predict the position of the stationary points for the XFH^+/FX' reactions studied by Pross and Radom.[24] The F–H bond orders are determined from Pauling's relationship, ("*a*" in eq 17 is defined by setting $n = {}^1/_2$ for the identity reaction[15b]), and these bond orders are assumed to give a good approximation to $X^{\ddagger}$ and to $1 - X^{\ddagger}$. Equations 19 and 21 are then employed (using the approximation $^1/_2[1 + h_1(X^{\ddagger})] = X^{\ddagger}$) to obtain predicted values of $X^{\ddagger}$ and $1 - X^{\ddagger}$. Table VI shows that bond order is conserved in the intermediates to within a maximum deviation of 0.05, and Miller's relationship yields a better prediction of both $X^{\ddagger}$ and $1 - X^{\ddagger}$ than does the Marcus model.

It is interesting that the Miller equation for the barrier position gives a prediction of $X^{\ddagger}$ closer to the SCF value than the Marcus equation whenever single-minimum reaction coordinates are examined (Table IV and VI). For the double-minima reaction coordinates (Table IV), the Marcus equation appears to be more accurate. The limited number of examples prevents a more detailed analysis of this observation, but it may be significant that the curvature of h_1 near $X = 0$ and $X = 1$ is distinctly different for the two types of reaction coordinate (compare Figures 1, 4, and 7 and Figures 12 and 16). The effect of curvature in h_1 on deviations of $X^{\ddagger}$ from the Marcus or Miller predictions has been discussed previously.[15d]

VII. Conclusions

It has been shown that the breakdown of the Marcus equation, as it is usually applied, is due, in part, to the nonadditivity of the intrinsic barriers in certain systems. Another important factor is deviation from the "square" relationship (i.e., $h_2 = h_1^2$). In the present examples, a mixed quartic function gives an excellent prediction of barrier height, position, and shape in the cases where the reaction coordinate can be expressed in terms of three stationary points (i.e., reactants, transition state or intermediate, and products). The fact that the "intrinsic" component of the cross reaction may be the average of the corresponding identity components and that h_2 is strongly dominated by the quadratic and quartic contributions is particularly significant and may indicate that many chemical processes are describable as first- or low-order perturbations. This speculation will be explored in future work.[15,21]

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Supplementary Material Available: Table I, optimized geometries and energies of reactants, intermediates, and products of $HF/^{-}OH$, $HCl/^{-}OH$, H_3O^+/PH_3 systems, and Appendix I, geometry optimizations for FHF^-, $HOHOH^-$, $FHOH^-$, $ClHCl^-$, $ClHCl^-$, $ClHOH^-$, $PH_3HPH_3^+$, $PH_3HOH_2^+$, and $H_2OHOH_2^+$ and potential surfaces and reaction coordinates (9 pages). Ordering information is given on any current masthead page.

The Application of Marcus-like Equations to Processes Which Have No Corresponding Identity Reactions. Separation of Thermodynamic and Intrinsic Contributions to Barriers to Internal Rotation and Conformational Rearrangements

Morgan Y. Chen and Joseph R. Murdoch*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received September 17, 1982*

Abstract: In the past, there has been extensive interest in applying the Marcus equation to electron-, atom-, proton-transfer reactions, nucleophilic substitutions, and other types of group-transfer reactions (e.g., $A{-}B + C \rightarrow A + B{-}C$) which are associated with related identity reactions (e.g., $A{-}B + A \rightarrow A + B{-}A$ and $C{-}B + C \rightarrow C + B{-}C$). The barriers of the identity reactions can be used to obtain the *intrinsic* barrier of the unsymmetrical reaction, which allows a prediction of the barrier for the unsymmetrical reaction ($\Delta E_{AC}^{\ddagger}$) from the intrinsic barrier ($\Delta E_0^{\ddagger} = {}^1/_2[\Delta E_{AA}^{\ddagger} + \Delta E_{CC}^{\ddagger}]$) and the overall thermodynamics of the reaction (ΔE). The separation of barriers into *intrinsic* and *thermodynamic* components facilitates a comparison of barriers for reactions of different thermodynamics and allows isolation of factors contributing to the reaction barrier that are unrelated to the reaction thermodynamics. Previously, the application of the Marcus equation to reactions that are not associated with identity reactions has been hampered due to the lack of any independent method for obtaining the intrinsic barrier. In the present paper, a new method is presented for obtaining the intrinsic barrier for an arbitrary reaction. The method is applied to 338 computed and experimental barriers to internal rotation, and it is shown that the barriers to internal rotation are well-described by the overall thermodynamics of the rotation and the intrinsic barrier through equations similar to the Marcus equation. It is demonstrated that a principle reason for the success of the Marcus-like equations in predicting barrier heights and positions is that the portion of the reaction coordinate covering three stationary points (reactant, transition state or stable intermediate, product) is closely represented by a low-order Fourier series. This feature suggests that Marcus-like equations can be successfully employed for predicting barrier heights and barrier positions for processes that have no associated identity reactions (e.g., pericyclic reactions and addition–eliminations). The results, as well as previous work, suggest that simple extensions of the Marcus equation can be used as a general model for chemical reactivity which encompasses both transition states and stable intermediates along the reaction coordinate.

I. Introduction

A. Barriers to Internal Rotation and General Rate–Equilibrium Expressions. Several approaches are currently in use for approximating activation energies of reaction pathways, including equations by London–Eyring–Polanyi–Sato (LEPS),[1] Johnston and Parr,[2] Marcus,[3] Murdoch and Magnoli,[4a,b] Rehm and Weller,[5] Agmon and Levine,[6] Bell,[7] le Noble,[8] Lewis,[9] Kurz,[10] Thornton,[11] Zavitsas,[12] and Ahrland–Chatt–Davies–Williams.[13] All these

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