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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

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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 → A + B–C) which are associated with related identity reactions (e.g., A–B + A → A + B–A and C–B + C → 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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quantitative expressions for the barrier height can be shown to be special cases, or extensions, of eq 1,[4c] where ΔE is the thermodynamic energy difference between reactants and products, g_1 and g_2 are odd and even functions of τ, and $\Delta E_0^\ddagger$ is the intrinsic barrier.[3]

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

These various expressions for the barrier height differ only by the choice of functions $g_1(\tau)$ and $g_2(\tau)$ in eq 1. For example, when $g_1(\tau) = \tau = {}^1/_4\Delta E/\Delta E_0^\ddagger$ and $g_2(\tau) = \tau^2$, Marcus' equation

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

is the result.

A reaction coordinate can be described in terms of a general energy expression,[4d] eq 3.

$$E(X) = E'(X) - E'(0) = \Delta E_0^\ddagger(1 - h_2(X)) + \tfrac{1}{2}\Delta E(1 + h_1(X)) \qquad (3)$$

$E'(X)$ is the energy at a given displacement (X) along the reaction coordinate where $h_1(X)$ and $h_2(X)$ are odd and even functions of X, respectively, about $X = {}^1/_2$, ΔE is the thermodynamic energy difference between reactants and products, and $\Delta E_0^\ddagger$ is the intrinsic barrier of the reaction. Note that

$$0 \le X \le 1 \qquad (4)$$

$$\Delta E = E'(1) - E'(0) = E(1) \qquad (5)$$

$$\Delta E_0^\ddagger = E'(\tfrac{1}{2}) - E'(0) - \tfrac{1}{2}\Delta E = E(\tfrac{1}{2}) - \tfrac{1}{2}\Delta E \qquad (6)$$

$$h_2(\tfrac{1}{2}) = 0 \qquad (7)$$

$$\Delta E_0^\ddagger \neq 0,\ h_2(1 - X) = h_2(X) \qquad (8)$$

$$\Delta E \neq 0,\ h_1(1 - X) = -h_1(X) \qquad (9)$$

Equation 3 gives the energy as a function of distance along the reaction coordinate, while eq 1 gives the barrier height as a function of ΔE and $\Delta E_0^\ddagger$. Equations 1 and 3 have previously been applied to electron-, proton-, atom-, and group-transfer reactions,[4,14-17] as well as pericyclic reactions.[4e,f]

B. Reaction Coordinates. Dissection into Intrinsic and Thermodynamic Contributions. For $\Delta E \neq 0$ and $\Delta E_0^\ddagger \neq 0$, $E(X)$ (the difference between the energy at X and the energy at 0) can be divided into an even, intrinsic (or kinetic) component and an odd, thermodynamic component.[4a] The value of the intrinsic (kinetic) component at the maximum or minimum is the intrinsic barrier, and can be related to whether a reaction is *kinetically* or thermodynamically controlled.[4a-c] An example of how an arbitrary reaction coordinate can be dissected into its even and odd components is illustrated in Figure 1.[4g,h]

We will assume that the reaction coordinate is a continuous function of X ($0 \le X \le 1$), and it can be expanded in a Taylor series about $X = {}^1/_2$. The Taylor series expansion for $E(X)$ will contain odd and even powers of $(X - {}^1/_2)$. Similarly, $E(1 - X)$ can be expanded into odd and even powers about $X = {}^1/_2$. When X is replaced by $1 - X$, the odd terms in the expansion for $E(1 - X)$ have the same magnitude, but the opposite sign, as the corresponding terms in the expansion for $E(X)$.[4d] The even terms in $E(X)$ and $E(1 - X)$ are identical.[4d] With use of $\mathcal{O}(X)$ to symbolize the sum of the odd terms in $E(X)$ and $\mathcal{E}(X)$ to symbolize the sum of the even terms in $E(X)$,

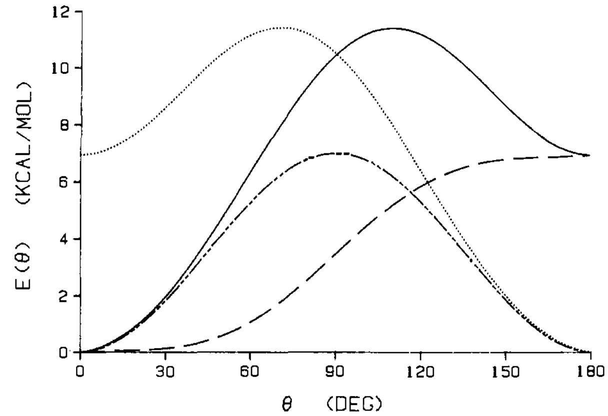

Figure 1. The reaction coordinate, $E(\theta)$, is represented by the solid line, and $E(1 - \theta)$ is given by the dotted line. $E(\theta)$ can be divided (eq 10 to 18) into an even, intrinsic contribution (−···−) and an odd thermodynamic contribution (– – –). The thermodynamic component measures the propagation of ΔE across the reaction coordinate while the intrinsic component indicates the magnitude of the barrier in the absence of a thermodynamic difference between the two rotomers. This particular example is CH_3NHOH.

$$E(X) = \mathcal{O}(X) + \mathcal{E}(X) \qquad (10)$$

$$E(1 - X) = -\mathcal{O}(X) + \mathcal{E}(X) \qquad (11)$$

Figure 1 and eq 10 and 11 show that $E(X)$ and $E(1 - X)$ are mirror images about $X = {}^1/_2$. Adding eq 10 and eq 11 leads to

$$\mathcal{E}(X) = \frac{E(X) + E(1 - X)}{2} \qquad (12)$$

while subtracting eq 11 from eq 10 yields

$$\mathcal{O}(X) = \frac{E(X) - E(1 - X)}{2} \qquad (13)$$

At $X = 0$,

$$\mathcal{E}(0) = \frac{E(0) + E(1)}{2} = +\tfrac{1}{2}\Delta E \qquad (14)$$

$$\mathcal{O}(0) = \frac{E(0) - E(1)}{2} = -\tfrac{1}{2}\Delta E \qquad (15)$$

The *intrinsic* contribution to $E(X)$ (i.e., the contribution independent of the overall thermodynamics) can be defined as

$$I(X) = \mathcal{E}(X) - \tfrac{1}{2}\Delta E \qquad (16)$$

while the *thermodynamic* contribution to $E(X)$ is

$$T(X) = \mathcal{O}(X) + \tfrac{1}{2}\Delta E \qquad (17)$$

$E(X)$, $E(1 - X)$, $I(X)$, and $T(X)$ are plotted in Figure 1. $E(X)$ can also be rewritten as

$$E(X) = \Delta E(S_1/2) + \tfrac{1}{2}\Delta E + \Delta E_0^\ddagger(S_2) \qquad (18)$$

where

$$S_1 = \frac{2\mathcal{O}(X)}{\Delta E} \text{ and } S_2 = \frac{(\mathcal{E}(X) - \tfrac{1}{2}\Delta E)}{\Delta E_0^\ddagger}$$

Setting $h_1 = S_1$ and $h_2 = 1 - S_2$ gives eq 3, which is a general expression for any barrier function where $\Delta E \neq 0$ and $\Delta E_0^\ddagger \neq 0$. Combining eq 6, 12, and 16, we find that $\Delta E_0^\ddagger = I({}^1/_2)$.

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C. The Marcus Equation and the "Square" Relationship. A special case of eq 3 is when $h_2(X) = h_1(X)^2$. If $E(X)$ is maximized or minimized with respect to X, Marcus' equation 2 results.[4d] Marcus' equation was originally derived for certain electron-transfer reactions by using the assumption that there is zero overlap between orbitals of the reacting species at the transition state. This weak overlap assumption would seem to be a poor description of any chemical process in which interactions are changing in going from reactants or products to the transition state. However, it has been shown that this condition of weak overlap is sufficient, but not necessary,[4a-c,18] and that a less restrictive condition is $h_2(X) = h_1(X)^2$ in eq 3.[4d] In previous work, this condition has been shown to be a fair approximation for group-transfer reactions[4,14-17] and for pericyclic reactions,[4e,f] and it would be of interest to explore the physical significance of $h_1(X)$ and the applicability of the "square" relationship to other reactions. In particular, the speculation that barriers to internal rotation and conformational reorganization can be described in terms of an intrinsic barrier and ΔE has no precedents in previous treatments of internal rotation[19] or in applications of the Marcus equation[4-18] to chemical reactivity. Consequently, as part of the effort to determine the limits of applicability of Marcus-like equations, an examination of barriers to conformational rearrangements seems especially worthwhile. In the present paper, the applicability of Marcus-like equations to internal rotation is demonstrated, and in section III, a sound theoretical basis for this applicability is presented.

II. Method

A. Potential Functions for Describing Internal Rotation. The potential functions used in this study have been taken from the literature and have been obtained from both SCF calculations and experimental spectroscopic measurements.[19] The general form of the potential function is

$$E(\theta) = \tfrac{1}{2}V_1(1 - \cos\theta) + \tfrac{1}{2}V_2(1 - \cos 2\theta) + \tfrac{1}{2}V_3(1 - \cos 3\theta) + V_1' \sin\theta + V_2' \sin 2\theta \quad (19)$$

where the V terms are constants and θ is the rotational angle relative to a specific reference point. The molecules investigated in this study along with each set of potential constants for eq 19 are listed in Table I. A typical potential curve is illustrated in Figure 2a.

B. Predictions of the Energies and Positions of Stationary Points Using the Marcus Equation. For each molecule, a plot of $E(\theta)$ vs. θ is divided into successive intervals that each contain only three local extrema, as indicated in Figure 2b. The energy function in each interval is divided into its *intrinsic* and *thermodynamic* contribution according to eq 16 and 17, and the intrinsic barrier, $\Delta E_0^{\ddagger}$, is determined from eq 6 or 16. When these derived intrinsic barriers and ΔE are used, barriers to internal rotation are estimated from Marcus' equation and a quartic extension,

$$\Delta E^{\ddagger} = \Delta E_0^{\ddagger} + \tfrac{1}{2}\Delta E + 9\Delta E^2/(2^7\Delta E_0^{\ddagger}) - 27\Delta E^4/(16^4\Delta E_0^{\ddagger 3}) \quad (20)$$

The estimated barriers are compared to the barrier E_{obsd}, calculated from eq 19. A sample of the results is listed in Table II and indicates the extent to which barriers to internal rotation can be described in terms of an intrinsic barrier and ΔE through Marcus-like equations.

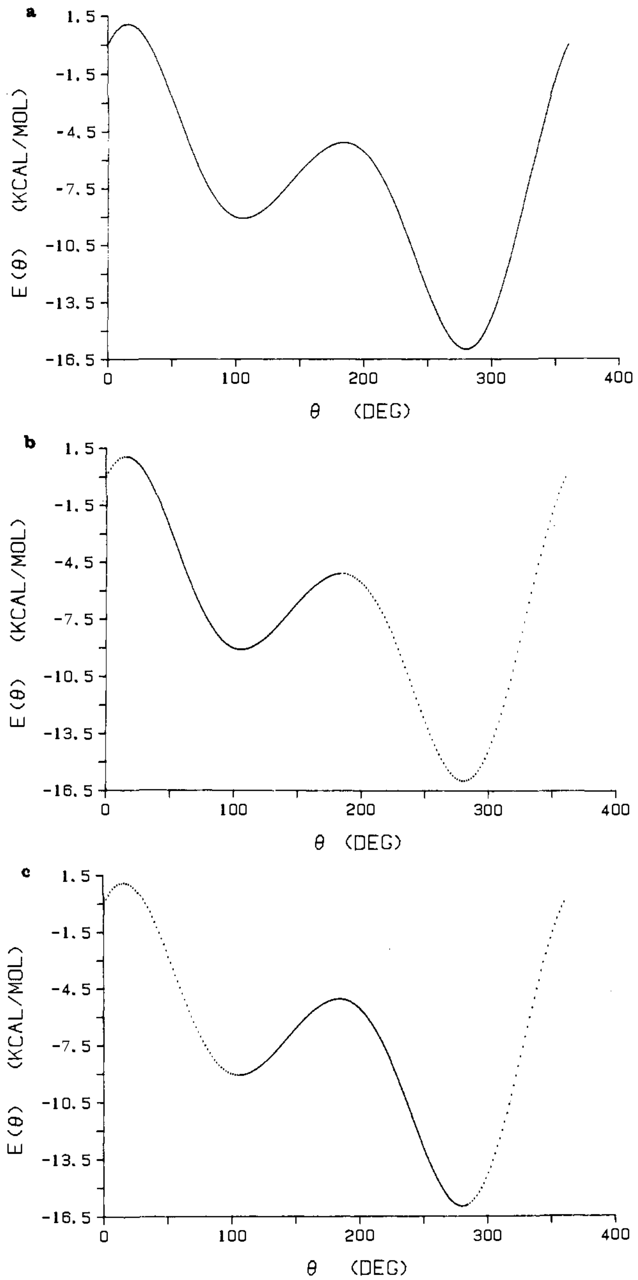

Figure 2. (a) The rotational potential curve of $FNHNH_2$. (b) The first interval of the potential curve includes three local extrema and is illustrated by the solid line. The interval may be dissected into even and odd components as in Figure 1 and $\Delta E_0^{\ddagger}$ and ΔE determined. (c) The next set of three local extrema is displayed, and the analysis indicated in Figures 1 and 2b is repeated.

The angles corresponding to the maximum and minimum energy states are obtained from eq 19 and are also estimated by using several approximations:[21]

$$X_{\text{Marcus}}^{\ddagger} = \frac{1}{2} + \frac{1}{8}\frac{\Delta E}{\Delta E_0^{\ddagger}} \quad (21)^{3,21}$$

$$X_{\text{Miller}}^{\ddagger} = \left(2 - \frac{\Delta E}{\Delta E^{\ddagger}}\right)^{-1} \quad (22)^{20,21}$$

$$X_{p=1/2}^{\ddagger} = \frac{\left(1 + \dfrac{\Delta E}{4\Delta E_0^{\ddagger}}\right)^2}{2\left(1 + \left(\dfrac{\Delta E}{4\Delta E_0^{\ddagger}}\right)^2\right)} \quad (23)^{4d,g,21}$$

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$$X_{p=2}^{\ddagger} = \frac{\left(1 + \frac{\Delta E}{4\Delta E_0^{\ddagger}}\right) - \left(1 - \left(\frac{1}{4}\frac{\Delta E}{\Delta E_0^{\ddagger}}\right)^2\right)^{1/2}}{\frac{1}{2}\frac{\Delta E}{\Delta E_0^{\ddagger}}} \qquad (24)^{4d,g,21}$$

$$X_{\text{arccos}}^{\ddagger} = \frac{1}{\pi}\arccos\left(-\frac{\Delta E}{4\Delta E_0^{\ddagger}}\right) \qquad (25)^{4d,21}$$

$$X_{p4}^{\ddagger} = \frac{1}{2} + \frac{3}{32}\frac{\Delta E}{\Delta E_0^{\ddagger}} \qquad (26)^{8,21}$$

Here the $X^{\ddagger}$'s are a fraction between $0 \leq X^{\ddagger} \leq 1$ and refer to the fractional displacement along the reaction coordinate. The values of $X^{\ddagger}$ are transformed back to the original scale in terms of θ by eq 27, and the θ values are listed in Table III. The process is

$$\theta_{i+1}^{\ddagger} = (\theta_{i+2} - \theta_i)X^{\ddagger} + \theta_i \qquad (27)$$

repeated, with the new interval starting at the next local extremum (see Figure 2c).

III. Discussion

A. The Marcus Equation Is Exact for 2-Fold Rotors. If only the first two terms in eq 19 are considered,

$$E(\theta) = \tfrac{1}{2}V_1(1 - \cos\theta) + \tfrac{1}{2}V_2(1 - \cos 2\theta) \qquad (28)$$

$$= \tfrac{1}{2}V_1(1 + (-\cos\theta)) + \tfrac{1}{2}V_2(1-(2\cos^2\theta - 1)) \qquad (29)$$

$$= \tfrac{1}{2}V_1(1 + (-\cos\theta)) + V_2(1 - \cos^2\theta) \qquad (30)$$

where $h_1^2 = (-\cos\theta)^2 = \cos^2\theta = h_2$, $V_1 = \Delta E$, $V_2 = \Delta E_0^{\ddagger}$, then the 2-fold rotor potential fits the square relationship, $h_1^2(X) = h_2(X)$, of eq 3 and thus Marcus' equation 2 predicts the barrier to internal rotation exactly. When more cosine and/or sine terms are added to eq 28, this may contribute to a deviation from $h_2(X) = h_1(X)^2$ and the Marcus equation may break down.

B. The Marcus Equation as an Interpolation Formula. Extensions. The Marcus equation 2 can be obtained from a quadratic interpolation scheme employing the second-order polynomial $P_2(X)$, which satisfies the conditions[22]

$$P_2(0) = E(0) \qquad (31)$$

$$P_2(\tfrac{1}{2}) = E(\tfrac{1}{2}) \qquad (32)$$

$$P_2(1) = E(1) \qquad (33)$$

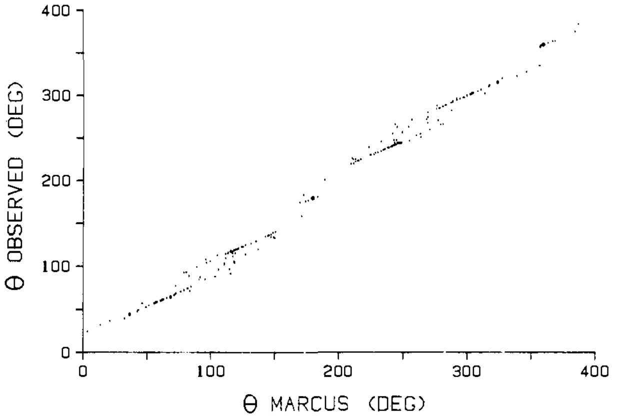

Figure 3. Correlation diagram between predicted values of reaction coordinate $\theta^{\ddagger}$ by using Marcus' equation 21 and those obtained through experiment or SCF calculation. The number of points is 338.

The error in Marcus' equation can be bound by the magnitude of the third derivative[22]

$$\max|\text{error}_{\text{Marcus}}| < \frac{1}{124}\left|E^{(3)}(\zeta)\right| \quad 0 \leq \zeta \leq 1 \qquad (34)$$

and thus Marcus' equation 2 will accurately predict activation energies for all energy functions $E(X)$ that are second order or lower.

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(21) Previous work defined a sigmoid function[4d]

$$h_1(X) = \frac{[X^P - (1 - X)^P]}{[X^P + (1 - X)^P]} \quad 0 \leq X \leq 1 \qquad (a)$$

where X is the reaction coordinate and $h_1(X)$ is defined above in eq 3. Setting $h_2(X) = h_1(X)^2$ in eq 3 and maximizing/minimizing $\Delta E^{\ddagger}(X)$ with respect to X lead to the condition

$$h_1(X^{\ddagger}) = \frac{1}{4}\frac{\Delta E}{\Delta E_0^{\ddagger}} \qquad (b)$$

Combining eq a and eq b, we obtain

$$\frac{1}{4}\frac{\Delta E}{\Delta E_0^{\ddagger}} = \frac{[X^{\ddagger P} - (1 - X^{\ddagger})^P]}{[X^{\ddagger P} + (1 - X^{\ddagger})^P]} \qquad (c)$$

Setting $P = 1$ and solving for $X^{\ddagger}$ gives the Marcus expression for $X^{\ddagger}$ (see ref 4d) eq 21, and $P = {}^1/_2$ gives the Miller relationship eq 22. Also shown is the case for $P = 2$. From eq 30 for a 2-fold rotor potential, we have $h_2(X) = h_1(X)^2$ and $h_1(X) = -\cos\Theta$ with $\theta = \pi X$. As before

$$h_1(X^{\ddagger}) = \frac{1}{4}\frac{\Delta E}{\Delta E_0^{\ddagger}} = -\cos\pi X^{\ddagger} \qquad (d)$$

Solving for $X^{\ddagger}$ gives eq 25. The approximation $X_{P_4}^{\ddagger}$ is obtained through maximizing/minimizing a fourth-order interpolant described in ref 23. For further details on eq a, please see ref 4d.

(22) We seek to determine the constants a, b, and c for $P_2(X) = a + bX + cX^2$ that satisfy eq 31–33.

$$P_2(0) = a = E(0) = 0$$

$$P_2(\tfrac{1}{2}) = a + (b/2) + (c/4) = E(\tfrac{1}{2})$$

$$P_2(1) = a + b + c = E(1)$$

Solving for a,b, and c in terms of $E(0)$, $E({}^1/_2)$, and $E(1)$ and then using the substitutions

$$\Delta E = E(1) - E(0)$$

$$\Delta E_0^{\ddagger} = -\tfrac{1}{2}E(0) + E(\tfrac{1}{2}) - \tfrac{1}{2}E(1)$$

leads to

$$P_2(X) = E(0) + (\Delta E + 4\Delta E_0^{\ddagger})X - 4\Delta E_0^{\ddagger}X^2$$

which satisfies the conditions of eq 31–33. Maximizing or minimizing $P_2(X)$ leads to

$$\mathrm{d}P_2(X)/\mathrm{d}X = 4\Delta E_0 + \Delta E - 8\Delta E_0^{\ddagger}X^{\ddagger} = 0$$

and the position for the maximum or minimum, eq 21, is obtained:

$$X^{\ddagger} = \frac{1}{2} + \frac{1}{8}\frac{\Delta E}{\Delta E_0^{\ddagger}}$$

Then

$$P_2(X^{\ddagger}) = \Delta E_0^{\ddagger} + \frac{1}{2}\Delta E + \frac{1}{16}\frac{\Delta E^2}{\Delta E_0^{\ddagger}} + E(0)$$

and

$$P_2(X^{\ddagger}) - E(0) = \Delta E^{\ddagger} = \Delta E_0^{\ddagger} + \frac{1}{2}\Delta E + \frac{1}{16}\frac{\Delta E^2}{\Delta E_0^{\ddagger}}$$

which is Marcus' equation 2. The error of an interpolating polynomial is

$$\text{err}(X) = E(X) - P_n(X) = \frac{f^{(n+1)}(\zeta)}{(n+1)!}\prod_{j=0}^{n}(X - X_j);\ 0 \leq \zeta \leq 1$$

where X_j are the interpolation points. For Marcus' equation $n = 2$

$$\text{err}(X) = \mathrm{E}(X) - P_2(X) = \frac{E^{(3)}(\zeta)}{3!}\prod_{j=0}^{2}(X - X_j)$$

$$\max|\text{err}(X)| \leq \frac{1}{6}\,|E^{(3)}(\zeta)|\max\left|X\left(X - \frac{1}{2}\right)(X - 1)\right| \leq \frac{1}{6}\left|E^{(3)}(\zeta)\right|\cdot\left|\frac{1}{36}3^{1/2}\right| =$$

$$\frac{3^{1/2}}{216}\left|E^{(3)}(\zeta)\right| \leq \left|\frac{E^{(3)}(\zeta)}{124}\right| \quad 0 \leq \zeta \leq 1$$

which is eq 34.

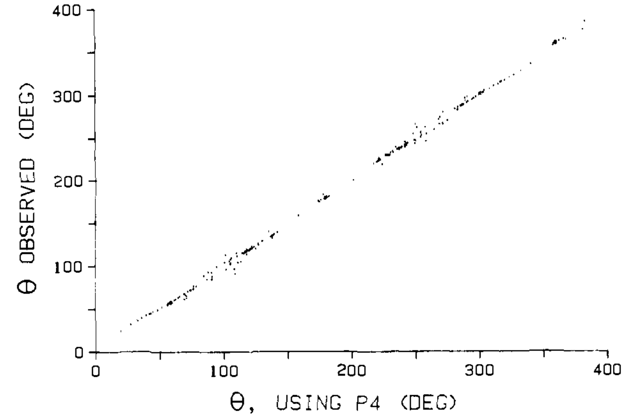

Figure 4. Correlation diagram between predicted values of reaction coordinates $\theta^{\ddagger}$ by using the quartic estimate equation 26 and those obtained through experiment or SCF calculation. The number of points is 338.

A higher order interpolation equation can be based on a quartic polynomial $P_4(X)$, which has the following constraints:[23]

$$P_4(0) = E(0) \tag{35}$$

$$P_4(\tfrac{1}{2}) = E(\tfrac{1}{2}) \tag{36}$$

$$P_4(1) = E(1) \tag{37}$$

$$P_4'(0) = P_4'(1) = 0 \tag{38}$$

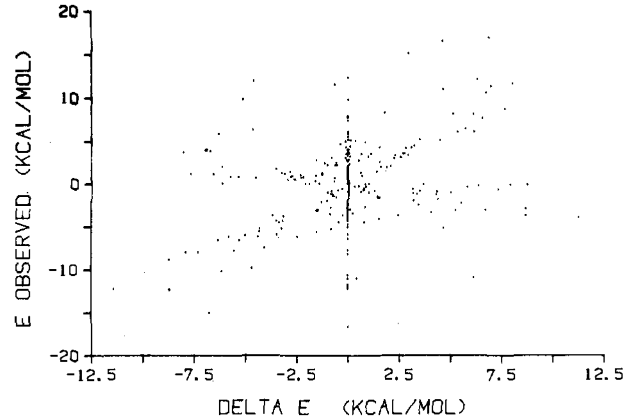

Figure 5. Plot of activation energy $\Delta E^{\ddagger}$ vs. ΔE. The number of points is 338.

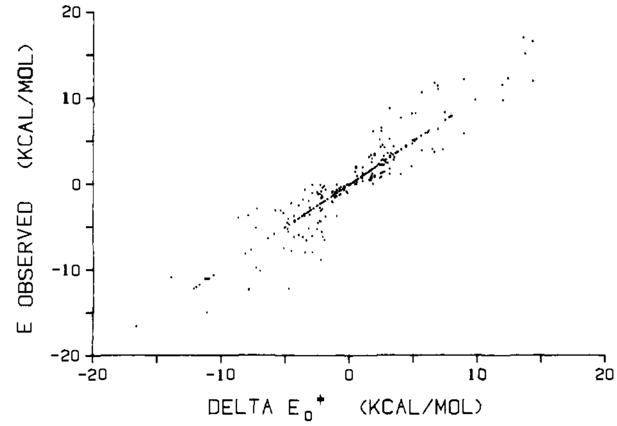

Figure 6. Plot of activation energy $\Delta E^{\ddagger}$ vs. the intrinsic barrier $\Delta E_0^{\ddagger}$. The number of points is 338.

where the new constraints imposed are that the slopes at the beginning and the end of the interval vanish. Note that for potential functions such as eq 19, $P_4'(0)$ and $P_4'(1)$ always equal zero. In other examples involving group-transfer reactions, the conditions do *not* hold,[48] and consequently, eq 38 should be replaced by an appropriate alternative. By use of eq 35–38, a fourth-order potential function can be obtained,[23] and from this, eq 20, the quartic extension can also be obtained. The error associated with eq 20 is given by[23]

$$\max|\mathrm{error}_{P_4}| < \frac{1}{13416}\left|E^{(5)}(\zeta)\right| \qquad 0 \leq \zeta \leq 1 \tag{39}$$

as long as the range $|(3/16)(\Delta E/\Delta E_0^{\ddagger})| \leq 1$ is obeyed. Due to the higher order interpolation scheme on which eq 20 is based and also due to the fact that the constraints of eq 35–38 are met by the potential surfaces generated from eq 19, it is not surprising that eq 20 gives more accurate results than the Marcus equation, particularly for values of $X^{\ddagger}$ (Figures 3, 4).

For $X^{\ddagger}$ close to $^1/_2$, all interpolation schemes work well, since the Taylor series error term $(X^{\ddagger} - {}^1/_2)$ becomes small. For values of $X^{\ddagger}$ away from $X^{\ddagger} = {}^1/_2$, the higher order interpolation, eq 20, would be expected to work better, as observed (Figures 3, 4).

In applying an interpolation scheme to predict energies associated with points on a potential surface, it is important to recognize that an *n*th-order interpolation formula is *not* equivalent to keeping the terms up to *n*th order in a Taylor series expansion of the exact potential surface. It is widely known[24] that *n*th, or even lower, order polynomials can often be found that give a substantially better fit over the entire domain of the function than

---

(23) We seek to determine

$$P_4(X) = a + bX + cX^2 + dX^3 + fx^4$$

which satisfies eq 35–38.

$$P_4(0) = a = E(0) = 0$$

$$\mathrm{P}_4(\tfrac{1}{2}) = a = \frac{b}{2} + \frac{c}{4} + \frac{d}{8} + \frac{f}{16} = E(\tfrac{1}{2})$$

$$P_4(1) = a + b + c + d + f = E(1)$$

$$P'_4(0) = b = 0$$

$$P'_4(1) = b + 2c + 3d + 4f = 0$$

Solving for *a*, *b*, *c*, *d*, and *f* in terms of $E(0)$, $E(^1/_2)$, and $E(1)$ and using the substitutions

$$\Delta E = E(1) - E(0)$$

$$\Delta E_0^{\ddagger} = -{}^1/_2E(0) + E(\tfrac{1}{2}) - \tfrac{1}{2}E(1)$$

lead to

$$P_4(X) = E(0) + (3\Delta E + 16\Delta E_0^{\ddagger})X^2 - (2\Delta E + 32\Delta E_0^{\ddagger})X^3 + 16\Delta E_0^{\ddagger}X^4$$

which satisfies the constraints of eq 35–38. Maximizing or minimizing $P_4(X)$ leads to

$$\mathrm{d}P_4(X)/\mathrm{d}X = 2(3\Delta E + 16\Delta E_0^{\ddagger})X - 3(2\Delta E + 32\Delta E_0^{\ddagger})X^2 + 64\Delta E_0^{\ddagger}X^3 = 0$$

which has $X^{\ddagger} = 0$, $^1/_2 + {}^3/_{32}\,\Delta E/\Delta E_0^{\ddagger}$, and 1 as solutions. Then,

$$P_4\left(X^{\ddagger} = \frac{1}{2} + \frac{3\,\Delta E}{32\,\Delta E_0^{\ddagger}}\right) - E(0) = \Delta E^{\ddagger} = \Delta E_0^{\ddagger} + \frac{1}{2}\Delta E + \frac{9}{128}\frac{\Delta E^2}{\Delta E_0^{\ddagger}} - \frac{27}{65336}\frac{\Delta E^4}{\Delta E_0^{\ddagger 3}}$$

which is eq 20. The associated error is

$$\mathrm{err}\ (\mathrm{X}) = E(X) - P_4(X) = \frac{E^{(5)}(\zeta)}{5!}\prod_{j=0}^{4}(X - X_j)$$

$$\max|\mathrm{err}\ (X)| \leq \frac{1}{120}\ |E^{(5)}(\zeta)|\max|X{\cdot}X\left(X - \frac{1}{2}\right)(X - 1)(X - 1)|$$

$$\leq \frac{1}{120}\left|E^{(5)}(\zeta)\right|\frac{5^{1/2}}{250} = \frac{5^{1/2}}{30000}\ |E^{(5)}(\zeta)|$$

$$\leq \frac{1}{13416}\ |E^{(5)}(\zeta)| \qquad 0 \leq \zeta \leq 1$$

which is eq 39.

(24) B. Carnahan, H. A. Luthor, and J. D. Wilkes, "Applied Numerical Methods", Wiley, New York, 1969.

(25) For a general discussion of obtaining intrinsic barriers from $\Delta E^{\ddagger}$ and ΔE measurements see (a) J. R. Murdoch, *J. Am. Chem. Soc.* **94**, 4410 (1972). (b) J. R. Murdoch, *J. Am. Chem. Soc.* **102**, 71 (1980). (c) J. R. Murdoch, *J. Phys. Chem.*, **87**, 1571 (1983). (d) J. R. Murdoch, unpublished data.

Table I. Potential Constants (kcal/mol) Obtained in the Literature[a]

molecule	V_1	V_2	V_3	V_1'	V_2'	ref
$CH_3CH_2NH_2$	0.89	0.21	−2.29			19a
FCH_2NH_2	−4.86	4.28	−2.01			19a
CH_3CH_2OH	−0.93	−0.05	−1.14			19a
FCH_2OH	5.25	−2.20	−0.96			19a
NH_2NH_2	−7.42	−7.92	−1.27			19a
CH_3NHNH_2	−6.84	−7.56	−1.85	−0.34	−0.12	19a
$FNHNH_2$	−3.70	−9.50	−1.40	3.50	2.14	19a
NH_2OH	8.86	6.62	−0.84			19a
NH_2OCH_3	8.47	5.65	−1.75			19a
NH_2OF	−3.67	14.30	−0.94			19a
CH_3NHOH	8.03	6.65	−1.08	0.35	0.16	19a
FNHOH	4.46	7.50	−0.83	−4.09	−1.40	19a
HOOH	−7.08	−3.51	−0.22			19a
CH_3OOH	−7.53	−2.94	−0.37			19a
FOOH	4.20	−5.17	−0.13			19a
$LiCH_2OH$	−5.10	2.05	−1.27			19c
$HBeCH_2OH$	−5.67	0.51	−1.23			19c
H_2BCH_2OH (perp)	−3.81	−1.15	−1.32			19c
H_2BCH_2OH (copl)	−1.50	1.69	−1.00			19c
$LiCH_2NH_2$	4.76	−3.40	−2.34			19c
$HBeCH_2NH_2$	4.81	−1.10	−2.29			19c
$H_2BCH_2NH_2$ (perp)	3.11	1.54	−2.43			19c
$H_2BCH_2NH_2$ (copl)	1.45	−2.37	−2.18			19c
$(COF)_2$	0.08	4.90	0.29			19g
COFCOCl	−0.18	3.14	0.30			19g
$(COCl)_2$	2.86	0.87	2.04			19g
HOCHO	5.75	8.93	0.55			19f
CHOCHO	5.73	4.85	0.40			19f
CH_3CH_2CHO	0.70	0.23	0.59			19f
propanol	−1.02	−1.02	−4.53			19h
ethyl methyl ether	−5.19	−1.53	−3.16			19h
$CH_3CH_2FH^+$	−0.614	0.765	−0.380			19l
$CH_3CH_2C{\equiv}CCH_2CH_3$	-1.67×10^{-2}	-4.78×10^{-3}	9.56×10^{-3}			19d,e
$CH_3CH_2CH_2CH_3$	−3.19	−1.43	−3.86			19d,e
$CH_3CH_2C{\equiv}CCH_2F$	7.41×10^{-2}	7.17×10^{-3}	7.17×10^{-3}			19d,e
$CH_3CH_2CH_2F$	-4.80×10^{-1}	-6.07×10^{-1}	−4.67			19d,e
$CH_3CH_2C{\equiv}CCH_2Li$	-6.93×10^{-2}	4.06×10^{-2}	1.91×10^{-2}			19d,e
$CH_3CH_2CH_2Li$	0.507	0.624	−3.28			19d,e
$FCH_2C{\equiv}CCH_2F$	−0.777	−0.837	4.78×10^{-3}			19d,e
FCH_2CH_2F	−4.68	−2.72	−4.09			19d,e
$LiCH_2C{\equiv}CCH_2Li$	−3.11	−1.90	-2.87×10^{-2}			19d,e
$LiCH_2C{\equiv}CCH_2F$	1.53	1.71	2.39×10^{-2}			19d,e
$LiCH_2CH_2F$	7.62	6.89	−2.98			19d,e
$H{-}C{\equiv}CCH_2NH_2$	−2.36	1.23	−1.84			19i
$N{\equiv}CCH_2NH_2$	−1.69	2.25	−1.79			19i
$H_3SiCH_2NH_2$	3.97	6.93×10^{-2}	−2.01			19j,k,l
$Me_3SiCH_2NH_2$	4.18	0.108	−2.12			19j,k,l
$H_3GeCH_2NH_2$	4.92	0.715	−2.36			19j,k,l
$CH_3CH_2OH_2{}^+$	1.64	−0.497	−1.03			19j,k,l
$H_3SiCH_2OH_2{}^+$	7.28	0.760	−1.76			19j,k,l
$Me_3SiCH_2OH_2{}^+$	6.79	0.533	−1.81			19j,k,l
$H_3GeCH_2OH_2{}^+$	9.73	1.46	−2.17			19j,k,l
$CH_3CH_2CH_2F$(exp)	−3.22	−3.05	−6.48			19b
FCH_2CH_2F(exp)	−3.23	−2.66	−2.90			19b
$CH_3CH_2CH_2NH_2$ (conf IV)	2.57	−0.863	−1.57			19j,k,l
$H_3SiCH_2CH_2NH_2$ (conf IV)	2.50	−0.903	−1.59			19j,k,l
$H_3GeCH_2CH_2NH_2$ (conf IV)	2.53	−0.951	−1.58			19j,k,l
$CH_3CH_2CH_2F$	0.920	0.951	−2.33			19j,k,l
$CH_3CH_2CH_2NH_2$	0.249	−0.222	−2.45	0.158	0.153	19j,k,l
$H_3SiCH_2CH_2NH_2$	−4.06	−2.95	−3.63	0.612	0.576	19j,k,l
$H_3GeCH_2CH_2NH_2$	−9.04	−6.06	−5.18	1.13	1.06	19j,k,l
CH_3CH_2OH	−2.03	0.559	−0.731			19j,k,l
$CH_3CH_2CH_2NH_2$ (conf V)	3.07	−0.633	−1.58	−0.232	-7.65×10^{-2}	19j,k,l
$H_3SiCH_2CH_2NH_2$	2.50	−0.903	−1.59			19j,k,l
$H_3SiCH_2CH_2NH_2$	4.75	−0.447	−1.45			19j,k,l
$H_3GeCH_2CH_2NH_2$	2.53	−0.951	−1.58			19j,k,l
$CH_3CH_2CH_2OH$	−2.35	0.688	−0.758			19j,k,l
$H_3SiCH_2CH_2OH$	−2.13	0.681	−0.727			19j,k,l
$H_3GeCH_2CH_2OH$	−2.13	0.739	−0.722			19j,k,l

[a] Some Constants may be slightly different than those from the original source due to rounding.

the *n*th order Taylor series expansion.

An important result of the present work is the finding that the section of a potential energy surface spanning only three stationary points may be well-described by a quadratic or quartic interpolation technique, even though the equation generating the overall surface (e.g., eq 19) contains higher order terms (e.g., V_3, V_1', V_2', etc.). This property of the surfaces examined in the present and previous[4g,h] papers is the fundamental reason behind the success of the Marcus equation, and its extensions, in correlating barrier heights and positions through an intrinsic barrier and ΔE.

Table II. A Sample of $\Delta E^{\ddagger}$ vs. $\Delta E^{\ddagger}$ Predicted by Using Marcus' equation 2 and the Quartic Extension Equation 20 along with the Values of ΔE and $\Delta E_0^{\ddagger}$ Used to Calculate Them[a]

molecule	start of interval	$\Delta E_{\mathrm{obsd}}^{\ddagger}$	$\Delta E_{\mathrm{Marcus}}^{\ddagger}$	$\Delta E_{\mathrm{P_4}}^{\ddagger}$	$\Delta E_0^{\ddagger}$	ΔE
$FNHNH_2$	15.8	−10.2	−10.4	−10.5	−7.02	−6.15
	106	4.01	4.27	4.31	7.30	−6.88
	184	−10.9	−11.1	−11.1	−14.0	6.15
	280	17.0	17.2	17.3	13.6	6.88
$LiCH_2NH_2$	0	−3.73	−3.21	−3.22	−4.35	2.46
	63.3	6.19	6.19	6.25	1.81	6.15
	159	−0.04	−0.04	−0.04	−0.04	0
$CH_3CH_2CH_2F$(exp)	0	−9.83	−9.85	−9.87	−7.33	−4.67
	67.4	5.16	5.16	5.16	5.09	0.13
	123	−5.03	−5.03	−5.03	−5.03	0
FCH_2CH_2F(exp)	0	−6.16	−6.18	−6.22	−3.67	−4.38
	74.2	1.78	1.78	1.78	1.76	0.03
	125	−1.75	−1.75	−1.75	−1.75	0
CH_3CH_2CHO	0	0.984	0.977	0.983	0.578	0.695
	70.8	−0.289	−0.281	−0.282	−0.420	0.306
	117	0.595	0.595	0.595	0.595	0
$H_3GeCH_2NH_2$	0	−0.938	−0.860	−0.909	−2.56	4.32
	45.3	5.25	5.11	5.14	3.12	3.50
	127	−1.76	−1.76	−1.76	−1.76	0

[a] All energies are in kcal/mol. All angles shown are in degrees.

Table III. A Sample of $\theta^{\ddagger}$ vs. $\theta^{\ddagger}$ Predicted by Using Eq 21-26[a]

molecule	$\theta_{\mathrm{obsd}}^{\ddagger}$	$\theta_{p=1}^{\ddagger}$	$\theta_{p=1/2}^{\ddagger}$	$\theta_{\mathrm{arccos}}^{\ddagger}$	$\theta_{p=2}^{\ddagger}$	$\theta_{p_4}^{\ddagger}$	$\theta_{\mathrm{Miller}}^{\ddagger}$
$FNHNH_2$	106	118	135	112	109	114	136
	184	172	154	180	183	178	153
	280	269	259	273	275	272	259
	376	385	396	381	379	382	396
$LiCH_2NH_2$	63.3	68.3	57.4	72.3	73.9	71.1	59.7
	159	171	179	159	154	159	179
	180	180	180	180	180	180	180
$CH_3CH_2CH_2F$ (exp)	67.4	71.2	80.5	67.7	66.3	68.7	80.5
	123	124	124	124	124	124	124
	180	180	180	180	180	180	180
FCH_2CH_2F (exp)	74.2	81.3	96.9	74.7	72.2	76.7	97.2
	125	127	127	127	127	127	127
	180	180	180	180	180	180	180
CH_3CH_2CHO	70.8	76.3	91.0	70.1	67.7	71.9	90.7
	117	115	106	119	120	118	106
	180	180	180	180	180	180	180
$H_3GeCH_2NH_2$	45.3	36.8	18.1	46.0	49.5	43.5	19.2
	127	132	148	125	122	127	146
	180	180	180	180	180	180	180

[a] All numerical entries are in degrees.

There appear to be three, and possibly more, factors related to the success of the low-order interpolation techniques: (1) it has been found[4,18] that many chemical and structural perturbations can apparently be described in terms of first- or low-order perturbations to the wavefunction; (2) it has been shown[4d,e,g] that expressing the perturbation in terms of a transformed variable (e.g., bond order[4e,g] or Fourier functions) rather than in Cartesian coordinates[4e,g] or in degrees may simplify the order of the perturbation; and (3) it is known[24] that low-order polynomials can often be found[18c,d] that give a better approximation to a function over its entire domain than does a high-order Taylor's expansion. In view of recent results,[4,18] these questions concerning the role of high-order terms in chemical and structural perturbations have assumed some significance and will be addressed in more detail in future work.

C. Correlations of Energy Barriers. It is interesting to note that the plot (Figure 5) of $\Delta E^{\ddagger}$ vs. ΔE is a scatter diagram: there is no obvious *general* correlation of barrier heights with the corresponding thermodynamics of going from one rotamer to another. The plot of $\Delta E^{\ddagger}$ vs. $\Delta E_0^{\ddagger}$ (Figure 6) shows a rough qualitative correlation, but it is clear that ΔE or $\Delta E_0^{\ddagger}$ *alone* do not determine the barrier height. However, ΔE and $\Delta E_0^{\ddagger}$ together give a good representation of the barriers to internal rotation through the Marcus equation or the quartic extension (Figures 7, 8).

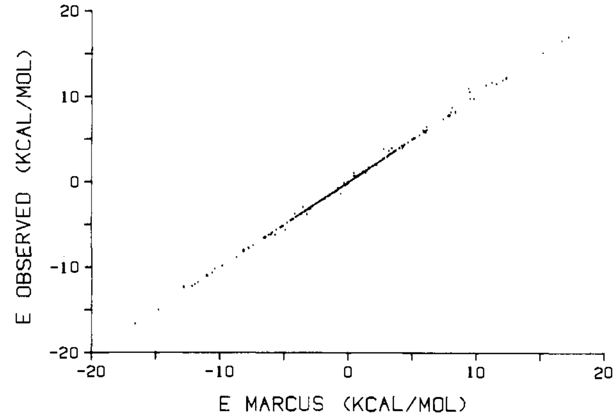

Figure 7. Plot of activation energies $\Delta E^{\ddagger}$ obtained through experiment or SCF calculations vs. predicted activation energies by Marcus' equation 2. The number of points is 338.

D. Thermodynamic Limits. Finite or Infinite? Marcus' equation 2 and the quartic extension equation 20 express the barrier height or well depth for a reaction in terms of the intrinsic barrier $\Delta E_0^{\ddagger}$ and the thermodynamics of the reaction, ΔE. It is instructive to note that the barrier approaches ΔE from above for

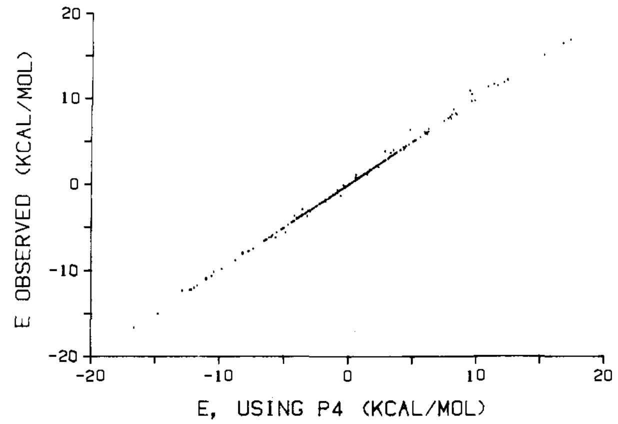

Figure 8. Plot of activation energies $\Delta E^{\ddagger}$ obtained through experiment of SCF calculations vs. predicted activation energies by using the quartic extension equation 20. The number of points is 338.

Table IV. Some Examples Where the Barrier $\Delta E^{\ddagger}$ Approaches ΔE for a Finite Ratio $\Delta E/\Delta E_0^{\ddagger}$ [a]

molecule	interval	$\Delta E_0^{\ddagger}$	ΔE	$\Delta E/\Delta E_0^{\ddagger}$
H_3SiCH_2OH	0–92.2	−0.154	−3.25	21.0
	92.2–180	8.0×10^{-2}	−2.73	−34.2
Me_3SiCH_2OH	0–91.8	−0.171	−3.26	19.0
	91.8–180	0.108	−2.83	−26.3
H_3GeCH_2OH	0–96.3	−0.241	−4.68	19.4
	96.3–180	-6.4×10^{-3}	−2.92	45.4
$H_3GeCH_2FH^+$	0–113	−0.240	−9.96	41.4
	113–180	−0.458	−3.15	6.9
$Me_3SiCH_2FH^+$	0–97.4	6.9×10^{-2}	−5.20	−75.1
	97.4–180	−0.254	−3.39	13.3
$H_3SiCH_2FH^+$	0–104	2.3×10^{-2}	−6.42	−27.7
	104–180	−0.347	−3.00	8.6
$LiCH_2OH$	0–74.3	−0.107	−1.06	9.9
	74.3–180	0.884	−5.31	−6.0
$HBeCH_2OH$	0–85.8	-8.6×10^{-2}	−2.87	33.3
	85.8–180	0.259	−4.03	−15.5

[a] All energies are in kcal/mol. All angles shown are in degrees.

endothermic reactions as $\Delta E \rightarrow 4\Delta E_0^{\ddagger}$ and equals ΔE when $\Delta E = 4\Delta E_0^{\ddagger}$. Likewise, for exothermic reactions, the barrier approaches 0 from above as $\Delta E \rightarrow -4\Delta E_0^{\ddagger}$. Consequently, the Marcus equation predicts a barrier to reaction in both directions for

$$-4|\Delta E_0^{\ddagger}| < \Delta E < 4|\Delta E_0^{\ddagger}| \tag{40}$$

In similar fashion, one can show that the quartic polynomial also places limits on the range of ΔE for which a barrier to reaction in both directions will exist:

$$-\frac{16}{3}\left|\Delta E_0^{\ddagger}\right| < \Delta E \ \frac{16}{3}\left|\Delta E_0^{\ddagger}\right| \tag{41}$$

There is some uncertainty of the behavior of $\Delta E^{\ddagger}$ when ΔE departs from these limits, and a discussion of this has been presented.[4i] However, the point to which we wish to draw attention is the suggestion from some authors[26a–d] that $\Delta E^{\ddagger} \rightarrow \Delta E$ only when $\Delta E/\Delta E_0^{\ddagger} \rightarrow \infty$. We list in Table IV various molecules where the limiting behavior is observed for finite values of $\Delta E/\Delta E_0^{\ddagger}$. Criteria for observing finite or infinite limits have been given previously.[4b]

IV. Conclusions

A. The Marcus Equation Applies to Conformational Equilibria. The intrinsic barrier concept is rapidly gaining recognition as the keystone in unravelling the complexities of structure–reactivity relationships for proton-transfer reactions,[4] S_N2 substitution,[14–17] pericyclic reactions,[4e,f] E2 eliminations,[4e] and others.[4d] We can now add internal rotational and conformational equilibria to this list.

B. Intrinsic Barriers to Conformational Changes. The fact that the Marcus equation, or simple extensions, gives accurate descriptions of barriers to internal rotation is an important result, since eq 2 (or eq 20) can be used to convert a measured (or calculated) value of $\Delta E^{\ddagger}$ and ΔE into an intrinsic barrier without having to evaluate the entire reaction coordinate. The barrier height ($\Delta E^{\ddagger}$) and the corresponding value of ΔE are sufficient to obtain the intrinsic barrier.[25] The fact that the reaction barrier has a dependence on the overall thermodynamics of the reaction and that this dependence can be separated from intrinsic contributions, unrelated to the thermodynamics, is a significant result and should be useful in comparing barriers to internal rotation when the energy difference between the initial and final rotamers is a variable.

C. Group Contributions to Intrinsic Barriers. The fact that the Marcus equation gives a good description of the barriers and is associated with a second-order description of the potential surface is also a significant result. In previous work, it has been shown that at the Hartree–Fock level,[18] second-order energy corrections, due to interchanging structural fragments between a series of molecules, can be rigorously associated with contributions from individual fragments. These contributions can be additive or nonadditive,[18] and an important, but untested, implication is that changes in intrinsic barriers due to structural perturbations can be described in terms of group or fragment contributions. Such a result would permit the evaluation of intrinsic barriers for all reactions in a fashion analogous to that presently is use for group-transfer reactions where the intrinsic barrier for $A–B + C \rightarrow A + B–C$ is obtained by averaging the barriers for the thermoneutral reactions $A–B + A \rightarrow A + B–A$ and $C–B + C \rightarrow C + B–C$. Each identity reaction makes an independent contribution to the intrinsic barrier of the unsymmetrical reaction.

D. Extension of the Intrinsic Barrier Concept beyond Group-Transfer Reactions. The present application of the Marcus equation and the quartic extension to conformational rearrangements marks the first time that the intrinsic barrier concept has been successfully applied to reactions that have no associated identity reactions. The fundamental basis behind the present application lies in the relationship between the function $h_1(x)$ and the function $h_2(x)$ in eq 3. The "square" relationship ($h_2(x) = h_1(x)^2$) leads to the Marcus equation for barrier heights, and one common example of the "square" relationship occurs in the form of the 2-fold rotor potential. For higher order potential surfaces, the "square" relationship still holds to a high degree over the portions of the potential surface which encompass three stationary points (e.g., reactant, transition state, product), and it is found that a quartic extension is an even better description.[27] An important point is that the specific form of h_1 or h_2 has no effect on the relationship between $\Delta E^{\ddagger}$, $\Delta E_0^{\ddagger}$, and ΔE. The key factor is how h_1 and h_2 are related to each other, and the specific relationship between h_1 and x, or between h_2 and x, is entirely irrelevant with respect to predicting barrier heights from the Marcus equation or the quartic extension. Consequently, any reaction coordinate that can be transformed to a quartic in *some* variable will give a barrier height described by eq 20.[28] Since many transformations of x are conceivable, it is quite likely that the Marcus equation and the higher order extensions will find extensive applications to a wide variety of chemical reactions, none of which could be anticipated on the basis of Marcus' original derivation[3] for electron-transfer reactions or on the basis of the existing extensions and variations.[1,2,4–17,26] Important points that require further work include the nature and physical significance

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(27) For the quartic polynomial, $P_4(X)$, which is given in ref 23, $h_1(X) = -1 + 6f(X)^2 - 4f(X)^3$, $h_2(X) = 1 - 16f(X)^2[1 - f(X)]^2$, and $f(X)$ is arbitrary. For the present application, $X = [\theta - \theta_R]/[\theta_P - \theta_R]$ (see eq 27) and $f(X) = X$.

(28) Earlier work by Kurz (ref 10) is especially relevant to the concept of using coordinate transformations to generalize barrier relationships.

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Table V[a]

line	R	A	B	χ^2	σ_A	σ_B	σ
E^b vs. ΔE	0.307287	9×10^{-7}	0.18835	9.38	0.1651	3.2×10^{-2}	0.13504
E vs. $\Delta E_0^\ddagger$	0.94727	-2×10^{-2}	0.866336	2.3569	8.2×10^{-2}	1.6×10^{-2}	5×10^{-2}
E vs. E_{p4}	0.99914	-4×10^{-2}	0.993422	5×10^{-2}	1.2×10^{-2}	2.2×10^{-3}	6×10^{-3}
E vs. E_{Marcus}	0.999096	-4×10^{-2}	0.990536	5×10^{-2}	1.2×10^{-2}	2.3×10^{-3}	7×10^{-3}
X^c vs. X_{p4}	0.999568	0.2540	0.998808	8.981	0.3809	1.6×10^{-3}	8×10^{-3}
X vs. X_{Miller}	0.987339	0.5574	0.997227	267.2	2.077	9×10^{-3}	4.1×10^{-3}
X vs. $X_{p=2}$	0.999282	0.1646	0.999241	14.94	0.4913	2×10^{-3}	1×10^{-2}
X vs. X_{arccos}	0.999566	9×10^{-2}	0.999552	9.03	0.3821	1.6×10^{-3}	8×10^{-3}
X vs. $X_{p=0.5}$	0.986496	0.238	0.998709	288.13	2.15	9×10^{-3}	4×10^{-2}
X vs. X_{Marcus}	0.998008	-2×10^{-2}	1.00007	41.6	0.819	3.4×10^{-3}	1.7×10^{-2}
theoretically	1.0	0.0	1.0	small	0.0	0.0	0.0

[a] A statistical fit to the line $y = A + Bx$ has the following associated parameters: A, constant term; B, linear coefficient; σ, standard deviation; σ_A, standard deviation in A; σ_B, standard deviation in B; R, correlation coefficient; and χ^2, chi square. [b] $n = 338$ for the E's. [c] $n = 338$ for the X's.

of transformations involving Cartesian-based coordinates as well as the relationship between the intrinsic barrier and quantities that form the basis of alternative treatments of chemical reactivity.

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Carbon–Carbon Bond Formation in the Reductive Coupling of Ketones by the Doubly Bonded Ditungsten(IV) Alkoxides $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$

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Abstract: Doubly bonded ditungsten(IV) alkoxides of the type $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$ promote the reductive coupling of certain ketones R′R″CO (R′ = Me; R″ = Me, Et, or University, to afford ditungsten(V) complexes of the type $W_2Cl_4(\mu\text{-}OR)_2[R'R''C(O)C(O)R'R'']_2$ (where R = Et or *n*-Pr, R′ = Me, and R″ = Me or Et) or the complex $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2[\text{Me-}n\text{-PrC(O)C(O)Me-}n\text{-Pr}]$ depending upon the choice of ketone. These are the first instances where multiply bonded dimetal complexes have been found to reductively couple ketones to form metal alkoxides derived from α-diols. Evidence is presented to support the notion that the role of the dimetal unit is to provide electrons for the reduction of the ketones and to serve as a template for the coupling of the resulting ketyl radicals. In the case of the formation of $W_2Cl_4(\mu\text{-}OR)_2[R'R''C(O)C(O)R'R'']_2$, it is believed that the following stoichiometric equation best explains the reaction course: $2W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2 + 4R'R''CO \rightarrow W_2Cl_4(\mu\text{-}OR)_2[R'R''C(O)C(O)R'R'']_2 + 4OR^- + 4ROH + 2\text{“}W^V\text{”}$. These complexes, which are derivatives of the singly bonded W_2^{10+} core, have been characterized by using cyclic voltammetry and ^{1}H NMR spectroscopy and, in the case of $W_2Cl_4(\mu\text{-}OEt)_2[R'R''C(O)C(O)R'R'']_2$ (R′ = Me; R″ = Me or Et), by X-ray crystallography. For $W_2Cl_4(\mu\text{-}OEt)_2[(CH_3)_2C(O)C(O)(CH_3)_2]_2$, crystals belong to the space group $P2_1/n$ with unit cell dimensions $a = 8.681$ (2) Å, $b = 15.743$ (3) Å, $c = 9.235$ (2) Å, $\beta = 90.98$ (2)°, $V = 1261.8$ (6) Å^3, and $Z = 2$. In these centrosymmetric molecules W–W = 2.701 (1) Å, W–OEt = 2.05 [2] Å, W–O$_T$ = 1.82 [1] Å, and W–Cl = 2.364 [7] Å. The conformation of the $\overline{\text{WWOCCO}}$ ring is unusual and indicates strain, but nevertheless, it is kinetically inert toward replacement by other RO$^-$ groups. $W_2Cl_4(\mu\text{-}OEt)_2[(CH_3)(C_2H_5)C(O)C(O)(CH_3)(C_2H_5)]_2$ also forms monoclinic crystals in space group $P2_1/n$ with unit cell dimensions $a = 10.660$ (10) Å, $b = 12.311$ (8) Å, $c = 11.268$ (9) Å, $\beta = 102.23$ (2)°, $V = 1452$ (2) Å^3, and $Z = 2$. The molecular dimensions are very similar to those for the first molecule. The methyl and ethyl groups are disordered in such a way as to indicate that there is little or no stereospecificity in the coupling of the $(CH_3)(C_2H_5)CO$ molecules.

The ditungsten(IV) alkoxides $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$[2,3] constitute the most extensive series of doubly bonded dimetal complexes so far discovered.[4] The most important chemical properties of this class of complexes are (1) the lability of the terminal OR and ROH ligands to exchange by other alcohol ligands,[3] (2) the ready displacement of the ROH ligands by other neutral donors, such as pyridine and other nitrogen donors,[5,6] and (3) their facile oxidation to the singly bonded ditungsten(V) alkoxides $W_2Cl_4(\mu\text{-}OR)_2(OR)_4$.[2,3,7] The latter two-electron oxidation proceeds formally with the loss of the two alcohol protons

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