

A Simple Relationship between Empirical Theories for Predicting Barrier Heights of Electron-, Proton-, Atom-, and Group-Transfer Reactions

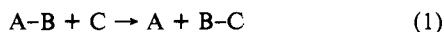
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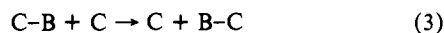
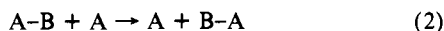
Abstract: In recent years there has been considerable interest in predicting the barriers to electron-transfer, proton-transfer, atom-transfer, and group-transfer (e.g., S_N2) reactions. In a previous paper, a simple equation was obtained that accurately predicts barrier heights for transition states and well depths for stable intermediates and is in agreement with a fair body of experimental data and ab initio potential energy surfaces. This equation has been obtained by using relationships describing the response of the electronic kinetic energy to perturbations and is not limited to any particular class of transfer reaction. In the present paper, it is shown that previous empirical equations (e.g., Marcus' equation, BEBO equation, LEPS equation, Rehm-Weller equation, Lewis' equation, Agmon-Levine equation, Bell's electrostatic model of proton transfer, le Noble's equation, Kurz's equation, etc.), obtained by a wide variety of apparently unrelated assumptions, are special cases of this more general result.

Introduction: Predicting Barriers and Well Depths for Group-Transfer Reactions

In the past few years there has been considerable interest in theoretical approaches to predicting barriers to reactions involving proton transfer or nucleophilic substitution. The Marcus equation,¹ originally derived for electron-transfer reactions, has been found to "work" surprisingly well for proton transfer and S_N2 reactions in the gas phase² and in solution.³ In a previous paper,⁴ it was shown that the Marcus equation also gives an accurate prediction (to within 1 kcal or so) of barrier heights calculated by SCF methods (Hartree-Fock or Hartree-Fock plus CI), and this finding led to an equation that has proved useful for estimating barriers⁴ and well depths^{4,5} for group-transfer reactions such as nucleophilic substitution^{4,6} and proton transfer.^{4,5} This equation describes the barrier (or well depth), ΔE_{AC}^{\ddagger} , for an unsymmetrical reaction



in terms of the barriers or well depths (ΔE_{AA}^{\ddagger} , ΔE_{CC}^{\ddagger}) for the corresponding identity reactions:



and the overall energy change, ΔE ,⁴ for reaction 1. ΔE_{AC}^{\ddagger} is given by

$$\Delta E_{AC}^{\ddagger} = \Delta E_0^{\ddagger}(1 - g_2) + \frac{1}{2}\Delta E(1 + g_1) \quad (4)$$

The functions g_1 and g_2 are odd and even functions^{4,5} of ΔE (or other specific parameters⁴) and govern the relative contributions of the kinetic term, $\Delta E_0^{\ddagger}(1 - g_2)$, and the thermodynamic term, $\frac{1}{2}\Delta E(1 + g_1)$, to the overall barrier or well depth.^{4,5} The intrinsic barrier,^{1,18,19} ΔE_0^{\ddagger} , is generally approximated as the average of the two identity barriers (i.e., $\Delta E_0^{\ddagger} = \frac{1}{2}[\Delta E_{AA}^{\ddagger} + \Delta E_{CC}^{\ddagger}]$), although exceptions may exist. For reactions near thermoneutrality

g_1 and g_2 are close to zero, giving

$$\Delta E_{AC}^{\ddagger} = \Delta E_0^{\ddagger} + \frac{1}{2}\Delta E \quad (5)$$

while for extremely exothermic reactions (large negative ΔE), $g_2 \rightarrow 1$ and $g_1 \rightarrow -1$, yielding^{4,5}

$$\Delta E_{AC}^{\ddagger} = 0 \quad (6)$$

In the case of highly endothermic reactions (large positive ΔE), $g_2 \rightarrow 1$, $g_1 \rightarrow 1$, and

$$\Delta E_{AC}^{\ddagger} = \Delta E \quad (7)$$

Such behavior conforms to that expected from Hammond's postulate⁷ and other qualitative proposals set down by Hughes, Ingold, and Shapiro,⁸ Bell, Evans, and Polanyi,⁹ Brønsted,¹⁰ Leffler,¹¹ Thornton,¹² More O'Ferrall,¹³ le Noble,¹⁴ Mok and Polanyi,¹⁵ and others. The purpose of the present paper is to point out that the quantitative barrier expressions given by London-Eyring-Polanyi-Sato (LEPS),¹⁶ Johnston and Parr,¹⁷ Marcus,^{1,18} Murdoch,¹⁹ Rehm and Weller,²⁰ Agmon and Levine,²¹ Bell,²² le Noble,¹⁴ Lewis,²³ Kurz,²⁴ Thornton,¹² Zavitsas,²⁵ and Ahrland-

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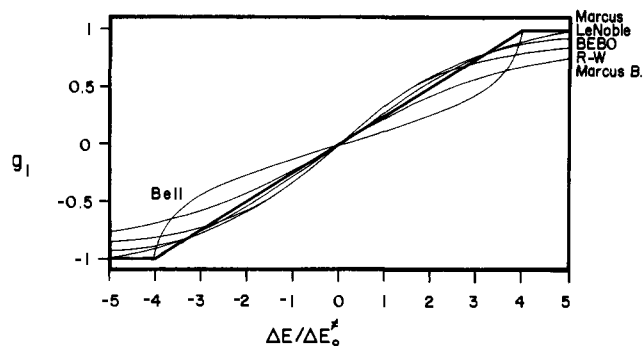


Figure 1. Behavior of g_1 for six empirical barrier functions. The g_1 corresponding to the Marcus equation is given by the heavy line, and the g_1 's corresponding to Le Noble's equation, the BEBO equation, the Rehm-Weller equation, and the Marcus-BEBO equation are identified by the upper right hand legend in the order corresponding to the respective values of g_1 at $\Delta E/\Delta E_0^\ddagger = 4.5$. The g_1 corresponding to Bell's electrostatic model of proton transfer is the sigmoid function, which terminates at $|\Delta E/\Delta E_0^\ddagger| = 4$ and is labeled "Bell". See Tables I and II.

Chatt-Davies-Williams²⁶ reduce to specific cases of eq 4 or to simple extensions.^{27,28} This result is of some significance, since all of these equations have enjoyed a high degree of empirical success and have not only been derived on the basis of widely divergent assumptions but frequently give excellent empirical correlations even when the underlying assumptions seem inapplicable. The previous derivation of eq 4⁴ is based on some simple properties of the kinetic energy²⁹ and is independent of the type of transfer reaction, the number of electrons involved in bonding,³⁰ and the size of transferred fragment. Consequently, it would be worthwhile to explore the relationship linking eq 4 to other empirical equations for electron-, proton-, atom-, or group-transfer reactions.

A Common Denominator

Eleven of the empirical equations can be shown to be special cases of eq 4, each of which corresponds to a different choice of g_1 and g_2 (Table I). For nearly thermoneutral reactions, all reduce to the first two terms of the Marcus equation (i.e., eq 5), which has been shown to be equivalent to an energy additivity relationship between the transition states for reactions 1, 2, and 3.^{5,31} It has also been shown that the breakdown from energy additivity can be approximated by proper choice of g_1 and g_2 .^{4,5} In Figures 1 and 2, a comparison is made of the various choices for g_1 and g_2 , and the resulting barriers (ΔE_{AC}^\ddagger) for reaction 1 are given in Table II. All equations give similar results for the range of $\Delta E/(4\Delta E_0^\ddagger)$ corresponding to many experimental reactions ($|\Delta E/(4\Delta E_0^\ddagger)| \leq 1$).³² The five essential ideas that follow from eq 4 are as follows:

- (1) A change in fragment (A, B, or C) for reaction 1 can be expected to alter both the kinetic term and the thermodynamic term. When changes in the kinetic term dominate and oppose changes in the thermodynamic term, the BEP principle⁹ is expected to fail and a less stable product may be formed faster than a more stable product.
- (2) When changes in the thermodynamic term and kinetic term are in the same direction or when changes in the thermodynamic term dominate, the BEP principle⁹ is expected to hold and the more stable product should be formed faster.

(26) S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J. Chem. Soc.*, 276 (1958).

(27) See eq 8.

(28) See footnote 55 in ref 4.

(29) J. R. Murdoch, *J. Am. Chem. Soc.*, **104**, 588 (1982).

(30) Group-transfer reactions usually involve cleavage of one bond and formation of another. In S_N2 or proton-transfer reactions, four electrons are formally associated with these two bonds, while three electrons are associated with the two bonds in atom transfer. Hydride transfer to a cation involves two electrons in a formal sense.

(31) (a) J. R. Murdoch, J. A. Bryson, D. F. McMillen, and J. I. Brauman, *J. Am. Chem. Soc.*, **104**, 600 (1982). (b) J. R. Murdoch, *ibid.*, **94**, 4410 (1972). (c) M. A. Ratner and R. D. Levine, *ibid.*, **102**, 4898 (1980).

(32) For a reaction with $\Delta E_0^\ddagger = 10$ kcal/mol, this range for ΔE would extend out to around ± 40 kcal/mol.

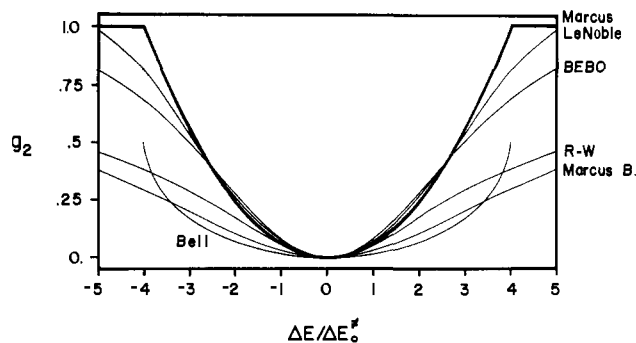


Figure 2. Behavior of g_2 for six empirical barrier functions. The g_2 corresponding to the Marcus equation is given by the heavy line and the others (see figure legend for Figure 1) are indicated by the appropriate label. The even function, g_2 , for the Rehm-Weller and Marcus-BEBO equations is arbitrary, and the term to the left of the plus sign of g_1 (see Table I) has been squared and set equal to g_2 for these two cases.

(3) As a thermoneutral reaction becomes more endothermic, the contribution of the kinetic term tends to decrease^{4,5} and the contribution of the thermodynamic term increases. A switchover from kinetic control to thermodynamic control may occur as the reaction becomes more endothermic and ΔE_{AC}^\ddagger approaches ΔE .

(4) As a thermoneutral reaction becomes more exothermic, the contributions of both thermodynamic and kinetic terms decrease, and ΔE_{AC}^\ddagger may approach 0.^{4,5} When $\lim g_2/g_1 = 0$ (as $\tau \rightarrow 0$; see Table I for examples), the thermodynamic term tends to decrease more quickly than the kinetic term, which may result in a switchover from thermodynamic to kinetic control as the reaction becomes more exothermic.

(5) The kinetic term [i.e., $\Delta E_0^\ddagger(1 - g_2)$] determines the relative barrier height for two reactions of comparable thermodynamics.

Extensions of Eq 4: Intrinsic Asymmetries

Two Sets of Interpolating Functions. The functions g_1 and g_2 can be interpreted⁴ as interpolating functions that transform the limiting case of additivity (eq 5) to the limit of eq 6 ($\Delta E_{AC}^\ddagger = 0$) or eq 7 ($\Delta E_{AC}^\ddagger = \Delta E$). It is also possible to use two sets of odd and even interpolating functions (e.g., $g_1^A, g_1^C, g_2^A, g_2^C$), so that a modified form of eq 4 results:⁴

$$\Delta E^\ddagger = \Delta E_0^\ddagger + V_A(\frac{1}{2} - f_A^\circ)g_2^A + V_C(\frac{1}{2} - f_C^\circ)g_2^C + \frac{1}{2}[\Delta E + V_A g_1^A - V_C g_1^C] \quad (8)$$

For proton-transfer reactions, V_A and V_C represent negative proton affinities,⁴ and f_A° and f_C° are related to the magnitude of the respective barriers for the identity reactions.^{1,33}

BEBO: Different Exponents. In the previous sections, the same exponent for the two bond order terms was used to describe a simplified BEBO model (Table I). If different exponents are used, then the BEBO equation

$$\Delta E^\ddagger = V_A - V_A(1 - n^*)^{p_A} - V_C(n^*)^{p_C} \quad (9)$$

can be transformed³⁴ to

$$\Delta E^\ddagger = \Delta E_0^\ddagger + \frac{1}{2}\Delta E + V_C \left[-\sum_{i=1}^{\infty} \frac{(p_C - 1)^i Q_i}{(i)!} \right] + V_A \left[-\sum_{i=1}^{\infty} \frac{(p_A - 1)^i Q_i}{(i)!} \right] + V_A \left[(n^* - \frac{1}{2}) + \sum_{i=1}^{\infty} \frac{(p_A - 1)^i R_i}{(i)!} \right] - V_C \left[(n^* - \frac{1}{2}) + \sum_{i=1}^{\infty} \frac{(p_C - 1)^i R_i}{(i)!} \right] \quad (10)$$

(33) The parameter f_A° relates V_A to the identity barrier through the equation, $\Delta E_{AA}^\ddagger = (2f_A^\circ - 1)V_A$. See eq 16, ref 4. Note that analogous quantities can be used for V_A in other types of group-transfer reactions: electron affinity (electron transfer); bond dissociation energy (atom transfer); methyl cation affinity (S_N2 at methyl); hydride affinity (hydride transfer); etc.

Table I. Evaluation of g_1 and g_2 for Empirical Barrier Functions

	equation	g_1	g_2	τ	(h)
1a. Marcus ¹	$\Delta E^\ddagger = \Delta E_0^\ddagger + 1/2\Delta E + \Delta E^2/16\Delta E_0^\ddagger$	τ	τ^2	$\Delta E/4\Delta E_0^\ddagger$	(b)
1b. Murdoch ¹⁹					
2. Thornton's inverted parabola ¹²					
3. Rehm-Weller ²⁰	$\Delta E^\ddagger = 1/2\Delta E + [(\Delta E_0^\ddagger)^2 + (1/2\Delta E)^2]^{1/2}$	$\frac{(1 + \tau^2)^{1/2} - 1}{\tau} + \frac{g_2(\tau)}{\tau}$	even ^a	$\Delta E/2\Delta E_0^\ddagger$	(c)
4. Lewis ²³					
5. Ahrland-Chart-Davies-Williams ²⁶					
6. Marcus-BEBO ¹⁸	$\Delta E^\ddagger = \Delta E_0^\ddagger + 1/2\Delta E + \frac{\Delta E_0^\ddagger}{\ln 2} \ln(\cosh \tau)$	$\frac{\ln \cosh \tau}{\tau} + \frac{g_2(\tau)(\ln 2)}{\tau}$	even ^a	$\frac{\Delta E \ln 2}{2\Delta E_0^\ddagger}$	(d)
7. Agmon-Levine ²¹					
8. Bell's electrostatic model ²²	$\Delta E^\ddagger = \frac{(n^\ddagger - p)^2}{Lp(1-p)(1-2n^\ddagger + 2n^{\ddagger 2})}$ $= \Delta E_0^\ddagger \frac{1}{1+4\tau^2} + 1/2\Delta E \left(1 + \frac{\tau}{1-2p}\right)$ $n^\ddagger = 1/2 + \tau$ $L = \text{distance between centers of two spheres with radius } pL \text{ and total charge of } L^{22}$	$\tau/(1-2p)$	$\frac{4\tau^2}{1+4\tau^2}$	$n^\ddagger - 1/2 =$ $\frac{1 - \Delta E'}{1 - \Delta E' + (1 - \Delta E'^2)^{1/2}} - \frac{1}{2}$ $\Delta E' = -1/2\Delta E(1-2p)/\Delta E_0^\ddagger$	(e)
9. BEBO (simplified) ¹⁷	$\Delta E^\ddagger = V_A - V_A(1-n^\ddagger)^p - V_C(n^\ddagger)^p$ $n^\ddagger = 1/2 + \tau$	$2\tau + \sum_{i=1}^{\infty} \frac{(p-1)^i R_i}{(i)!} 2$ (see footnote i) or $n^{\ddagger p} - (1-n^\ddagger)^p$	$-2\sum_{i=1}^{\infty} \frac{(p-1)^i Q_i}{(i)! S_0}$ (see footnote i) or $\frac{1}{1-2(1/2)^p} [n^{\ddagger p} + (1-n^\ddagger)^p - 2(1/2)^p]$	$\frac{(V_A/V_C)^{1/(p-1)}}{1 + (V_A/V_C)^{1/(p-1)}} - \frac{1}{2}$	(f)
10. le Noble ¹⁴	$\Delta E^\ddagger = 16\Delta E_0^\ddagger n^4 - 2(\Delta E + 16\Delta E_0^\ddagger)n^3 + 3\left(\Delta E + \frac{16}{3}\Delta E_0^\ddagger\right)n^2$ $n = 1/2 + \tau$	$3\tau - 4\tau^3$	$8\tau^2 - 16\tau^4$	$\frac{3\Delta E}{32\Delta E_0^\ddagger}$	(g)
11. Kurz ²⁴	$\Delta E^\ddagger = 1/2[1 + 2(n^\ddagger - 1/2)]\Delta E + \Delta E_0^\ddagger [1 + \sum_{m \geq 1} b_m (n^\ddagger - 1/2)^{2m}]$ n^\ddagger is a root to the polynomial $0 = \Delta E + \Delta E_0^\ddagger \sum_{m \geq 1} 2mb_m (n - 1/2)^{2m-1}$	$2(n^\ddagger - 1/2)$	$\sum_{m \geq 1} b_m (n^\ddagger - 1/2)^{2m}$	$n^\ddagger - 1/2$	

^a Even function is arbitrary. ^b $|\Delta E/\Delta E_0^\ddagger| \leq 4$. ^c $|\Delta E/\Delta E_0^\ddagger| \leq \infty$. ^d $|\Delta E/\Delta E_0^\ddagger| \leq \infty$. ^e $|\Delta E/\Delta E_0^\ddagger| \leq 2/(1-2p)$; $p = 1/4$. ^f $|\Delta E/\Delta E_0^\ddagger| \leq 2/(1-2(1/2)^p)$; $\Delta E_0^\ddagger = 1/2(V_A + V_C) \cdot (1-2(1/2)^p)$.
^g $|\Delta E/\Delta E_0^\ddagger| \leq 32/6$. ^h See ref 4 and 5 for discussion of limiting behavior of $|\Delta E/\Delta E_0^\ddagger|$. ⁱ R_i is the sum of odd terms in the expansion of $n \ln^i n$; Q_i is the sum of even terms in the expansion of $n \ln^i n$ (excepting the zero-order term); $S_0 = \sum_i (p-1)^i 1/2/(i)!$.

Table II.^a Comparison of $\Delta E^\ddagger/\Delta E_0^\ddagger$ Vs. $\Delta E/\Delta E_0^\ddagger$

$\Delta E/\Delta E_0^\ddagger$	$\Delta E^\ddagger/\Delta E_0^\ddagger$ (Marcus)	$\Delta E^\ddagger/\Delta E_0^\ddagger$ (Rehm-Weller)	$\Delta E^\ddagger/\Delta E_0^\ddagger$ (Marcus-BEBO)	$\Delta E^\ddagger/\Delta E_0^\ddagger$ ^b (Bell)	$\Delta E^\ddagger/\Delta E_0^\ddagger$ ^c (BEBO)	$\Delta E^\ddagger/\Delta E_0^\ddagger$ (le Noble)
-4.0	0.0000	0.2361	0.0875		0.0777	0.0195
-3.5	0.0156	0.2656	0.1222	0.0238	0.1125	0.0495
-3.0	0.0625	0.3028	0.1699	0.0078	0.1609	0.0994
-2.5	0.1406	0.3508	0.2348	0.0791	0.2271	0.1734
-2.0	0.2500	0.4142	0.3219	0.2010	0.3160	0.2747
-1.5	0.3906	0.5000	0.4368	0.3595	0.4329	0.4061
-1.0	0.5625	0.6180	0.5850	0.5476	0.5830	0.5699
-0.5	0.7656	0.7808	0.7716	0.7618	0.7710	0.7676
0.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.5	1.2656	1.2808	1.2716	1.2618	1.2710	1.2676
1.0	1.5625	1.6180	1.5850	1.5476	1.5830	1.5699
1.5	1.8906	2.0000	1.9368	1.8595	1.9329	1.9061
2.0	2.2500	2.4142	2.3219	2.2010	2.3160	2.2747
2.5	2.6406	2.8508	2.7348	2.5791	2.7271	2.6734
3.0	3.0625	3.3028	3.1699	3.0078	3.1609	3.0994
3.5	3.5156	3.7656	3.6221	3.5238	3.6125	3.5495
4.0	4.0000	4.2361	4.0875		4.0777	4.0195

^a Values of $\Delta E^\ddagger/\Delta E_0^\ddagger$ for additional empirical functions are given in ref 4 and 5. ^b $p = 1/4$. ^c $p = 1.2$, $V_A = 100$ kcal/mol, $V_C = V_A - \Delta E$.

The nonadditive contribution to ΔE^\ddagger (see Table I for definitions of Q_i , R_i) consists of a weighted sum of V_A and V_C (kinetic term) and a weighted difference of V_A and V_C (thermodynamic term). The chief distinction between eq 8 and eq 4 is that ΔE^\ddagger will approach the limiting cases (eq 6 and 7) somewhat differently, since V_A and V_C are modified by different interpolating functions. Marcus has referred to this behavior as an intrinsic asymmetry,¹⁸ while Koepple and Kresge³⁵ have given specific examples.

BEBO: Different Exponents Plus Repulsion Term. The repulsion term in BEBO is given¹⁷ by

$$R_{AC} = D_e [1/2 e^{-\beta_0 \Delta r_s} (n_1 n_2)^{\beta_1}] [1 + 1/2 e^{-\beta_0 \Delta r_s} (n_1 n_2)^{\beta_1}] \quad (11)$$

The terms D_e , β_0 , Δr_s , β_1 refer to various properties of the A-C bond in the transition state corresponding to reaction 1 and are defined explicitly in the paper by Johnston and Parr.^{17,36}

Equation 11 can be simplified to³⁷

$$R_{AC} = D_{AC} C_{AC} [1/4 - \epsilon^2]^{\beta_1} + D_{AC} C_{AC}^2 [1/4 - \epsilon^2]^{2\beta_1} \quad (12)$$

where $D_{AC} = D_e$, $\epsilon = n^* - 1/2$, and $C_{AC} = 1/2 e^{-\beta_0 \Delta r_s}$. The expansion of $[1/4 - \epsilon^2]^{\beta_1}$ around $\epsilon = 0$ will contain only even terms in ϵ and will affect only the kinetic contribution to the barrier.

If the parameters in eq 12 are chosen to give the limiting case of eq 5, then³⁸

$$R_{AC} = (D_{AA} + D_{CC}) \left[\frac{(1 - n^*)n^*}{n_{01}^* n_{02}^*} \right]^\beta \left[1 + \left[\frac{(1 - n^*)n^*}{n_{01}^* n_{02}^*} \right]^\beta \right] \quad (13)$$

(34) This transformation is based on a Taylor series expansion of n^p to give: $n^p = n + n \ln n (p-1) + n \ln^2 n (p-1)^2/2! + \dots + n \ln^m n (p-1)^m/m!$. Substituting $n = 1/2 + \epsilon$ and $(1-n) = 1/2 - \epsilon$ and expanding $\ln^m n$ about $1/2$ gives $(1/2 + \epsilon)^p = (1/2 + \epsilon) + [Q_1 + R_1](p-1) + [Q_2 + R_2](p-1)^2/2! + \dots + [Q_m + R_m](p-1)^m/m!$ and $(1/2 - \epsilon)^p = (1/2 - \epsilon) + [Q_1 - R_1](p-1) + [Q_2 - R_2](p-1)^2/2! + \dots + [Q_m - R_m](p-1)^m/m!$. Q_i and R_i ($i = 1, m$) represent the odd and even terms, respectively, in the expansion of $n \ln^m n$ about $n = 1/2$. Substituting these expressions for $(1/2 + \epsilon)^p$ and $(1/2 - \epsilon)^p$ into eq 9 and collecting terms gives eq 10. Note that the bond order conservation condition ($n_1 + n_2 = 1$) plays an important role in the segregation of odd and even terms in the expansion.

(35) G. W. Koepple and A. J. Kresge, *J. Chem. Soc., Chem. Commun.*, 371 (1973).

(36) D_e = bond dissociation energy for A-C, β_0 = Morse constant for A-C bond, Δr_s = deviation of A-C bond length from the average of A-A and C-C bond lengths, $\beta_1 = 0.26\beta_0$. See ref 17 for more details.

(37) An important contribution to the simplicity of the final result is the bond order conservation condition imposed on BEBO: $n_1 + n_2 = 1$. This leads to $n_1 n_2 = (1/2 + \epsilon)(1/2 - \epsilon) = 1/4 - \epsilon^2$. The expansion of $[1/4 - \epsilon^2]^{\beta_1}$ about $\epsilon = 0$ will contain only even terms in ϵ .

(38) The limiting case of eq 5 requires that $R_{AC} = 1/2(R_{AA} + R_{CC})$ when $(1 - n^*)$ and n^* for the cross reaction equals the corresponding quantities (n_{01}^* and n_{02}^* , respectively) for the associated identity reactions. When R_{AC} is chosen by some other criteria, nonadditive contributions to the intrinsic barrier (ΔE_0^\ddagger) may be significant even when $\Delta E \approx 0$. Similar remarks apply to eq 14 and 15.

After expansion of the exponential terms and use³⁹ of $D_{AA} = \chi_A V_A$ and $D_{CC} = \chi_C V_C$, it can be shown that R_{AC} divides into a weighted sum of V_A and V_C , where the weighting functions are even. $n \epsilon$.³⁷ The only effect of including the BEBO repulsion term is to modify the kinetic term of eq 10 without changing the general form. The fact that the general form of the BEBO equation is unchanged by addition of the repulsion term accounts for at least part of the observation that BEBO without repulsion and BEBO with repulsion often give similar results.¹⁷

Zavitsas Equation for Atom Transfers. The Zavitsas equation and extensive applications have been described in detail elsewhere.²⁵ The equation is applicable to atom-transfer reactions and can be reduced to the form⁴⁰

$$\Delta E^\ddagger = \Delta E_0^\ddagger + 1/2 \Delta E + [V_{AB} \epsilon_{AB}^2 + V_{BC} \epsilon_{BC}^2] + 1/4 F(\epsilon_{AB}, \epsilon_{BC})(V_{AB} \chi_{AB} + V_{BC} \chi_{BC}) + 2[V_{AB} \epsilon_{AB}(1 - n_{ABO}^*) - V_{BC} \epsilon_{BC}(1 - n_{BCO}^*)] \quad (14)$$

Since ϵ_{AB} and ϵ_{BC} are related by explicit transcendental equations,⁴¹ it can be shown that eq 14 is equivalent to an additive contribution (i.e., $\Delta E_0^\ddagger + 1/2 \Delta E$) plus a nonadditive contribution consisting of a weighted sum of V_{AB} and V_{BC} (kinetic term) and a weighted difference of V_{AB} and V_{BC} (thermodynamic term). Consequently the Zavitsas equation is also a special case of eq 8.³⁸

The LEPS Equation. The LEPS equation has been used extensively for fitting various experimental or theoretical data to functions describing potential surfaces of atom-transfer reactions.¹⁶ In the form obtained by Sato,^{16c} the LEPS equation can be expressed as⁴²

$$\Delta E^\ddagger = 1/2(D_{AB} + D_{AB}')n_{AB}^2 - (D_{AB} - D_{AB}')n_{AB} + 1/2(D_{BC} + D_{BC}')n_{BC}^2 - (D_{BC} - D_{BC}')n_{BC} + 1/2(D_{AC} + D_{AC}') \frac{(n_{AB}^{2a})(n_{BC}^{2b})}{C_0^2} - (D_{AC} - D_{AC}') \frac{n_{AB}^a n_{BC}^b}{C_0} - [(\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2]^{1/2} (1/2)^{1/2} + D_{AB} \quad (15)$$

(39) χ_A and χ_C are proportionality constants relating D_{AA} with V_A and D_{CC} with V_C , respectively.

(40) The Zavitsas equation (ref 25) can be written as $\Delta E^\ddagger = V_{AB} [n_{AB}^* (n_{AB}^* - 2) + 1] + V_{BC} [n_{BC}^* (n_{BC}^* - 2)] + V_{AC} [2n_{AB}^* n_{BC}^* / C_0 + n_{AB}^{2a} n_{BC}^{2b} / C_0^2]$ where $n_{AB}^* = e^{-\beta_{AB}(r_{AB}^* - r_{ABO})}$, β_{AB} is a Morse constant, r_{AB}^* is the A-B bond length in the A-B-C transition state, r_{ABO} is the equilibrium A-B bond length, V_{AB} , V_{BC} , and V_{AC} are bond dissociation energies, and C_0 is a constant. By use of $C_0 = n_{ABO}^* n_{BCO}^*$ (where n_{ABO}^* and n_{BCO}^* are bond orders (ref 43 and 44) corresponding to A-B and B-C in the appropriate identity reaction transition states) and expansion of the expression for ΔE^\ddagger about $n_{AB}^* = n_{ABO}^* - \epsilon_{AB}$ and $n_{BC}^* = n_{BCO}^* + \epsilon_{BC}$, eq 14 is obtained.

(41) Zavitsas uses an equibonding criterion (ref 25) to estimate the geometry and energy of the transition state. The exact quantities can be found by solving the equations $\partial \Delta E^\ddagger / \partial n_{AB} = 0$ and $\partial \Delta E^\ddagger / \partial n_{BC} = 0$ for n_{AB}^* and n_{BC}^* . As a result, ϵ_{AB} and ϵ_{BC} will be related so that each of them can be expressed as functions of common variables (bond dissociation energies, Morse parameters, etc.).

where D_{AB} and D_{BC} are bond dissociation energies of A-B and B-C, n_{AB} and n_{BC} are bond orders^{43,44} of the A-B and B-C bonds at the transition state,⁴⁵ and D_{AB}' , D_{BC}' , D_{AC} , D_{AC}' , a , b , and C_0 are adjustable constants.⁴⁶ The parameters α , β , and γ are given by

$$\alpha = \frac{1}{2}(D_{AB} - D_{AB}')n_{AB}^2 - (D_{AB} + D_{AB}')n_{AB} \quad (16)$$

$$\beta = \frac{1}{2}(D_{BC} - D_{BC}')n_{BC}^2 - (D_{BC} + D_{BC}')n_{BC} \quad (17)$$

$\gamma =$

$$\frac{1}{2}(D_{AC} - D_{AC}') \frac{(n_{AB}^{2a})(n_{BC}^{2b})}{C_0^2} - (D_{AC} + D_{AC}') \frac{(n_{AB}^a)(n_{BC}^b)}{C_0} \quad (18)$$

In the limiting case of $n_{AB} = 0$ and $n_{BC} = 1$, the LEPS equation reduces to

$$\Delta E^* = -D_{BC} + D_{AC} = \Delta E \quad (19)$$

which corresponds to one of the limiting cases of eq 4 (see eq 7). When $n_{AB} = 1$ and $n_{BC} = 0$, the LEPS equation simplifies to

$$\Delta E^* = 0 \quad (20)$$

which corresponds to another limiting case of eq 4 (see eq 6). For $\alpha \sim \beta$ and $(\alpha - \beta)^2 \ll (\alpha - \gamma)^2$ the LEPS equation reduces to the same thermoneutral limit as eq 1 (see eq 5).⁴⁷ Consequently, the LEPS equation and eq 4 share three important limiting cases (viz., eq 5-7), and for small changes in ΔE near $\Delta E = 0$, both equations give identical results.³⁸

These conclusions are based on first-order expansion of the square root term in eq 15, and it is instructive to briefly consider the second-order term,⁴⁸ which contains the factor $(\beta - \alpha)^2$. From eq 16 and 17 it can be seen that $(\beta - \alpha)^2$ will contain cross terms between D_{AB} and D_{BC} (i.e., $D_{AB}D_{BC}$). When $(\beta - \alpha)^2$ is expanded about $n_{AB} = n_{BC} = 1/2$, the even and odd terms in ϵ_{AB} and ϵ_{BC} ($1/2 + \epsilon = n$) can still be grouped together, as with BEBO and the Zavitvas equation but not all of the even and odd terms will be weighted by quantities related to properties associated with single bonds (e.g., V_{AB} and B_{BC} , eq 10 and 14). Consequently, the LEPS equation does not correspond precisely to a special case of eq 4 or eq 8, but all three equations exhibit similar behavior at and near⁴⁹ the limiting cases (i.e., eq 5-7).

Discussion and Conclusions

Elimination of Unnecessary Assumptions. The 14 empirical equations discussed in the present paper have been derived for the purpose of describing separate classes of group-transfer reactions, including electron transfer,^{1,20} atom transfer,^{14,16-19,23-25} proton transfer,^{14,19,22-26} and nucleophilic substitution.^{14,19,23,24} Not surprisingly, the assumptions on which these treatments are founded vary extensively. A significant contribution of the present work has been to demonstrate that all of these various treatments can be obtained from a common starting point (e.g., eq 4 or eq 8),^{4,5} which is not limited to any particular class of group-transfer reactions.

(42) The form of this equation is that given by Sato except that the coordinates are expressed in terms of bond order rather than Cartesian distances (see ref 43 and 44).

(43) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

(44) The Morse function [$D_e e^{-\beta(r-r_0)}(e^{\beta(r-r_0)} - 2)$] can be transformed from a distance variable (i.e., $r-r_0$) to a bond order variable (i.e., n) by making the substitution $n = e^{-\beta(r-r_0)}$. The Morse function is quadratic in bond order [$D_e n(n-2)$], and this property is useful in solving the Schrodinger equation for a Morse oscillator. Similar remarks apply to the anti-Morse function (see ref 16c).

(45) The parameters n_{AB} and n_{BC} in eq 15 represent values satisfying criteria for a stationary point (i.e., $\partial \Delta E^* / \partial n_{AB} = 0$ and $\partial \Delta E^* / \partial n_{BC} = 0$).

(46) For examples, see: (a) J. C. Polanyi and J. L. Schreiber, *Chem. Phys. Lett.*, **29**, 319 (1974). (b) A. F. Wagner, G. C. Schatz, and J. M. Bowman, *J. Chem. Phys.*, **74**, 4960 (1981).

(47) The term $[(\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2]^{1/2}(1/2^{1/2})$ is equivalent to $[(\alpha - \gamma)^2 + (\beta - \alpha)(\alpha - \gamma) + (\beta - \alpha)^2]^{1/2}$. Setting $\epsilon = (\beta - \alpha)(\alpha - \gamma) + (\beta - \alpha)^2$ and expanding about $(\alpha - \gamma)^2$ to first order, $[(\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2]^{1/2}(1/2^{1/2}) = 1/2\alpha + 1/2\beta - \gamma$. Substituting this expression in eq 15 for the two identity reactions and the cross reaction gives eq 5.

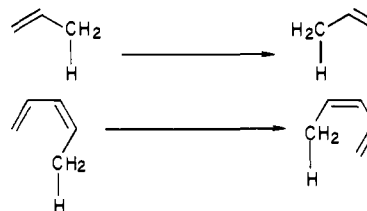
(48) $3/8(\beta - \alpha)^2/(\alpha - \gamma)$.

(49) For $\alpha, \gamma \rightarrow 0$, $[(\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2]^{1/2}(1/2^{1/2}) \approx \beta - 1/2(\alpha + \gamma)$. Substituting this equation into eq 15 yields eq 19 as $\alpha, \gamma \rightarrow 0$.

This is an important result, since many of these equations give reasonable results in spite of the fact that their underlying assumptions are often inappropriate. A good example is the Marcus equation, which was originally derived for electron-transfer reactions by assuming zero or weak overlap between the orbitals of the two reacting species in the transition state. The successful application of this equation to situations where the weak overlap approximation is clearly inapplicable (e.g., gas-phase proton transfers,^{4,5} S_N2 substitutions,^{2,4-6} and well depths of gas-phase proton-bound dimers^{4,5}) demonstrates that the assumptions suitable for certain electron-transfer reactions are sufficient but not necessary. Marcus used the weak overlap approximation to derive a "wave-function additivity" condition, and in three recent papers,^{4,5,29} it has been shown that this condition may still hold even when interactions between the reacting groups are substantial and changes in electronic structure have taken place. This example illustrates the important point that the assumptions supporting an empirical treatment may be of little consequence with regard to its usefulness in describing experimental results and the mathematical form following from the assumptions is far more significant.

Unusual Reactivity Patterns: Importance of Intrinsic Barriers and Kinetic Components. It has been widely recognized that reactions with comparable thermodynamics may exhibit substantial differences in their activation barriers.⁵⁰ Dispersion in rate-equilibrium correlations of proton-transfer reactions,⁵¹ the enhanced nucleophilicities (in terms of reaction rate constants) of second-row nucleophiles compared to first-row analogues,⁵¹ and the greater nucleophilicity often observed with nucleophiles containing lone pair(s) on the atom adjacent to the nucleophilic center (the α effect)⁵¹ provide some simple examples. For two reactions with different barriers and comparable thermodynamics, eq 4, 5, and 8 suggest that the barrier difference can be understood in terms of the corresponding identity barriers: the reaction with the lowest barrier should also correspond to the reaction with the lowest intrinsic barrier.⁵² For reactions with different thermodynamics, eq 4, 5, and 8 allow a prediction of the relative contribution of the kinetic and thermodynamic components to the overall barrier.

Orbital symmetry constraints are one factor that should affect the intrinsic barrier (ΔE_0^*) and the kinetic term [i.e., $\Delta E_0^*(1 - g_2)$]. Examples of group-transfer reactions subject to orbital symmetry constraints include sigmatropic rearrangements.⁵³ The



barriers to [1,5] shifts are generally lower than barriers to [1,3] shifts,⁵³ and these differences should appear as lower "intrinsic" barriers for the thermally allowed reactions (i.e., [1,5] shifts).

Catalysis is another fertile area for extending the idea of kinetic and thermodynamic contributions to reaction barriers. Catalysts are often described as agents that lower the energy of the transition state relative to reactants without altering the relative energy of reactants and products.⁵⁴ For a single-step group-transfer reaction, a catalyst could operate only by lowering the "intrinsic" barrier of the reaction.⁵⁵

(50) For leading references, see ref 4.

(51) Jerry March, "Advanced Organic Chemistry", McGraw-Hill, New York, 1977.

(52) For two unsymmetrical reactions (barriers given by ΔE_{AC}^* and ΔE_{DE}^*) there will be four identity reactions (barriers given by ΔE_{AA}^* , ΔE_{CC}^* , ΔE_{DD}^* , ΔE_{EE}^*). If the thermodynamics of reactions AC and DE are comparable, then the smaller barrier (ΔE_{AC}^* vs. ΔE_{DE}^*) will correspond to the lower average identity barrier [$1/2(\Delta E_{AA}^* + \Delta E_{CC}^*)$ vs. $1/2(\Delta E_{DD}^* + \Delta E_{EE}^*)$].

(53) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970.

(54) L. Pauling, *Am. Sci.*, **30**, 51 (1948).

The present paper and previous work^{4,5} have elaborated on the idea of kinetic and thermodynamic contributions to barriers of group-transfer reactions. The kinetic contribution [$\Delta E_0^*(1 - g_2)$] is related to the intrinsic barrier and depends upon the barriers of two identity reactions,¹ while the thermodynamic contribution [$1/2\Delta E(1 + g_1)$] derives from ΔE for the overall reaction. Both quantities can be obtained experimentally^{2,5,31a} or computed quantum mechanically.^{4,6} Equations 4 and 8 are compact ways of representing and predicting experimental data: n identity reactions provide sufficient information to calculate "intrinsic" barriers¹ for $n(n - 1)/2$ unsymmetrical group-transfer reactions. It should be noted that for other classes of reactions (e.g., carbonyl additions, cycloadditions, fragmentations, electrocyclic reactions), the separation of barriers into kinetic and thermodynamic contributions is still useful, although the quantitative formalism is somewhat different.^{5b}

(55) For multistep reactions, other factors may be important. For discussion, see: (a) J. R. Murdoch and D. E. Magnoli, *J. Am. Chem. Soc.*, **104**, 2782 (1982). (b) W. P. Jencks, *Chem. Rev.*, **72**, 705 (1972).

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(56) J. R. Murdoch, *J. Am. Chem. Soc.*, in press. The intrinsic barrier for any one-step reaction can be estimated from the Marcus equation by averaging the arithmetic and geometric means of the barriers in the forward and reverse directions. As the reaction approaches thermoneutrality, the arithmetic and geometric means converge and the intrinsic barrier is given by the average of the barriers for the forward and reverse directions. The intrinsic barrier from the Rehm-Weller equation corresponds to the geometric mean of forward and reverse barriers.

Paramagnetism and Antiaromaticity: Singlet-Triplet Equilibrium in Doubly Charged Benzenoid Polycyclic Systems

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Abstract: Fused benzenoid systems such as anthracene, phenanthrene, 3,4-benzophenanthrene, and chrysene were reduced with lithium, sodium, and potassium in various solvents to the antiaromatic doubly charged species. The NMR and ESR patterns of the dianions revealed a strong dependence on the counterion, solvent, and temperature. This dependence is interpreted by the existence of an equilibrium process between the singlet ground state and a thermally accessible excited triplet state of the antiaromatic dianions. The direction and extent of the equilibrium is determined by the energy gaps between the LUMO and HOMO of these charged species, which depends, in turn, on the topology of the hydrocarbon and on the solvation properties of the obtained salt.

Conjugated benzenoid polycyclic hydrocarbons undergo a 2-fold reduction process.² Scrutinized magnetic resonance studies, to be described below, performed on the resulting dianions reveal some hitherto unencountered phenomena that concern fundamental properties of antiaromatic charged systems. These phenomena point toward the existence of an equilibrium between the singlet ground state of the doubly charged benzenoid polycycles and a low-lying, thermally accessible excited triplet state. The equilibrium is found to have a substantial influence on the spectral patterns of these systems.

HMO considerations differentiate between two classes of ($4n + 2$) π -conjugated polycyclic species: systems endowed with C_3 or higher axial symmetry for which the highest occupied and lowest unoccupied orbitals appear in pairs vs. systems with lower axial

symmetry in which no such orbital degeneracies exist.³ The difference between the two classes becomes crucial when the polycycles are reduced to the corresponding ($4n$) π dianions. In the first group the two additional electrons populate two different degenerate orbitals, which may lead to a triplet ground state. This is the case in systems such as the triphenylene dianion (1),⁴ 1,3,5-triphenylbenzene dianion (2),⁵ and under strong solvating conditions the coronene dianion system (3).⁶ It should be noted that dianions of C_3 or a higher symmetry do not adopt by necessity a triplet ground state. Calculations have shown that configuration

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