is similar to that of other typical "organic" cations and, for example, the Gibbs free energy difference between water and acetonitrile, $\Delta G_{tr} = -9.8$ kJ mol^{-1}, of Ag(2,2,2)ClO_4 is comparable to that of Et_4NClO_4 ($\Delta G_{tr} = -4.2$ kJ mol^{-1}).[2] It is also noticeable that there is a minimum in ΔG_{tr} for Ag(2,2,2)ClO_4 around $x_{AN} = 0.6$, which presumably can be attributed to a slight preferential hydration of ClO_4^- as mentioned for $\Delta G_{tr}(AgClO_4)$, as the increase in ΔG_{tr}(Ag(2,2,2)ClO_4) on going from $x_{AN} = 0.5$ to pure acetonitrile is as large as that for $AgClO_4$. An extension of these studies to other cations and cryptands may lead to a more detailed explanation of the behavior of cryptates in solution.

Registry No. Ag(2,2,2)ClO_4, 80434-44-2; $KClO_4$, 7778-74-7; $AgClO_4$, 7783-93-9; (2,2,2), 23978-09-8.

Kinetic and Thermodynamic Control in Group Transfer Reactions

Joseph R. Murdoch* and Douglas E. Magnoli

Contribution from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received April 10, 1980*

Abstract: The concept of kinetic and thermodynamic control is basic to an understanding of chemical reactivity. In the present paper, a theory of nuclear substitution, developed in other work, is used to show that under certain conditions kinetic and thermodynamic factors can be rigorously separated for group transfer reactions (A–B + C → A + B–C). These factors can be evaluated from $\Delta E°$ for the overall reaction and from the barriers of two related "identity" reactions (A–B + A → A + B–A and C–B + C → C + B–C). For large values of $\Delta E°$, no rigorous separation is yet possible. However, using the virial theorem and the fact that the kinetic energy can be decomposed into orbital contributions, it is shown for proton-transfer reactions that the total energy expression at *stationary points* on the A–H–C potential surface (e.g., reactants, transition states, products) can be divided into two terms. In the limit of reactants (or products), one term reduces to the total energy of A–H (or A) and the other term corresponds to the total energy of C (or H–C). At other stationary points (viz., a transition state), it is shown that the two terms have altered values, but *no new terms are necessary to describe the interaction between the reacting molecules*. This convenient property is used to derive a simple empirical equation for the barrier of a group transfer reaction which takes the interplay of kinetic and thermodynamic factors into account. The general equation allows $\Delta E^{\ddagger}$ to approach $\Delta E°$ for sufficiently large, positive values of $\Delta E°$ (either finite or infinite), and special cases of the general expression can account for the SCF barriers of certain proton-transfer reactions to within 0.4 kcal over a range for $\Delta E°$ of 108 kcal.

The fact that rates and equilibria for chemical reactions often respond in similar fashion to changes in substituents has attracted considerable attention over the years. In the past, this connection has been approached from many different angles, and before introducing a new treatment, it would be instructive to examine some common elements which have emerged.

I. Introduction

A. Thermodynamic Factor—The Bronsted Relationship. In a large number of cases, a change in substituent which makes the reaction less favorable thermodynamically will also make the reaction proceed to equilibrium at a slower rate. This idea has a certain appeal and forms the basis for extensive theoretical and experimental work by a number of workers, including Bronsted,[1] Bell,[2] Evans and Polanyi,[3] Hammond,[4] Leffler,[5] Eigen,[6] and many others.[7]

At the transition state, it is commonly expected that the structural changes connecting reactants and products are at some intermediate stage of completion. Leffler[5] showed how this idea could lead to the quantitative form of Bronsted's catalysis law

$$\log k = \alpha \log K_{eq} + C \tag{1}$$

The central theme of Leffler's proposal is that if a substituent change destabilizes the products relative to the reactants, then some of this destabilization should carry over into the transition state since the transition state bears a partial, structural resemblance to the products. One implication of this hypothesis is that as a transition state approaches the products in structure, the destabilization of the transition state should approach the destabilization of the products, and α should approach unity.[7] The parameter α is regarded as a measure of the relative sensitivities of the transition state and the products to structural perturbations.[6,7] Equation 1 provides quantitative substance to the prevalent belief that the barrier of a reaction is dependent, in part, on the thermodynamics of the reaction. This dependence could be thought of as the thermodynamic component of the barrier.

B. Kinetic Factor. (1) Kinetic Acidity vs. Thermodynamic Acidity. Even though relationships such as the Bronsted equation (eq 1) tend to focus attention on the thermodynamic factor, it is widely recognized that other considerations are important as well. A simple example involves the deprotonation of a 2-methylcyclohexanone derivative by trityllithium.[8] Proton abstraction from the less hindered side is faster and results in initial formation of II, which slowly rearranges to the more stable enolate I. Similar "paradoxes" of the less stable product forming faster than the more stable product are well-known.[9]

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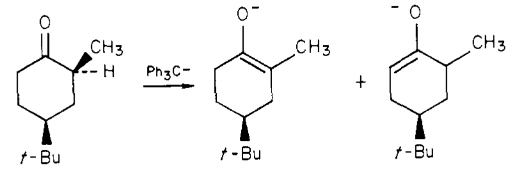

(2)

	I	II
kinetic product	14%	86%
thermodynamic product	89%	11%

(2) Deprotonation of Nitroalkanes. A second type of example which drew attention to this problem involves the base-catalyzed deprotonation of nitroalkanes. These reactions are unusual in that values of α greater than one (e.g., 1.7–1.9) or less than zero have been observed.[10] In one case the transition state is apparently *more* productlike than the products ($\alpha > 1$) and in the other, the transition state and products respond in opposite fashion to the same substituent changes! A similar result has been found in proton exchange reactions of 9-substituted fluorenes (vide infra, section IID1).

(3) Breakdown of the Rate-Selectivity Principle. A third important example deals with one of the corollaries associated with the Bronsted equation (eq 1): the rate-selectivity principle. A thorough discussion of its development has been given in a number of places,[7,11,12] but the idea derives from Hammond's proposal[4] that a transition state should bear a closer structural resemblance to the less stable side of a reaction coordinate. For a strongly endergonic reaction, the transition state is predicted[4] to resemble the products in structure, and according to the Bronsted equation, α should be close to one. For a strongly exergonic reaction, the transition state should resemble the reactants in structure, and such reactions should give small values of α near zero.[7] Reactions with small α's (i.e., fast, exergonic) are relatively unresponsive to changes in $\Delta G°$, while reactions with large α's (i.e., slow, endergonic) are strongly influenced by changes in $\Delta G°$. Consequently, if two competing reactions differ in their overall thermodynamics by a constant amount, then two slow reactions should show a larger difference in *relative* rate than two fast reactions. A number of examples are known where just the opposite result is obtained.[11-14]

The rate-selectivity principle derives from thermodynamic considerations. Its breakdown and the existence of reactions with anomalous α's ($\alpha > 1$ or $\alpha < 0$) point to the importance of additional factors which are present in the transition state but absent in the reactants or products.[10-19] These additional factors could be regarded as kinetic factors since they do not affect $\Delta G°$ for the reaction.

C. Origin of Kinetic and Thermodynamic Factors. (1) Pairwise Interaction Models—LEPS, BEBO, Zavitsas, Diatomics in Molecules. A reasonable empirical approach for predicting the barrier to a group transfer reaction (A–B + C → A + B–C) would be to approximate the energy of the complex, A–B–C, in terms of pairwise interactions between A–B, B–C, and A–C. The latter is clearly a kinetic factor since it is absent in the separated reactants and products,[15] while A–B and B–C interactions contain thermodynamic contributions relating to the A–B and B–C bond strengths in the isolated molecules.

The first attempt at deriving an A–B–C potential energy surface was based on an approximate quantum mechanical expression[20] for the energy of a three-body complex (A–B–C), where Morse and anti-Morse curves for A–B, B–C, and A–C were used to evaluate the various terms.[21,22] The BEBO method,[23] Zavitsas' method,[24] and diatomics in molecules (DIM)[25] were developed later and use different empirical schemes for obtaining the energy of the three-body complex. A striking aspect of these various formulations is that the calculated minimum energy pathway is in surprisingly good agreement with the results of ab initio calculations.[25-27]

(2) Intersecting Potential Functions. A second approach involves joining separate potential functions for the isolated reactants and products to produce a barrier function for the complex, A–B–C. In certain cases, the two potential functions are simply allowed to intersect,[2,3,27b,28,29] or some criterion is introduced to modify the potential functions as the transition state is approached.[27c,d,30-32] Reasonable results have been achieved in either case.[2,3,28-32]

(3) Hammond's Postulate and the Hughes–Ingold–Shapiro Principle. Related to LEPS,[20-21] BEBO,[23] and similar methods is a more qualitative suggestion by Hughes, Ingold and Shapiro,[17] which can be regarded as a generalization of Hammond's postulate.[4] Hughes, Ingold, and Shapiro[17] considered the effect of a perturbation on two arbitrary points of a potential surface. If two points are separated by an energy minimum and the energy of the first point (relative to the other) is raised by a perturbation, the position of the minimum will shift toward the second point. The opposite behavior will be observed for two points separated by a maximum. This effect is based on the analogous behavior of a parabolic minimum or maximum when a linear perturbation is added to the parabola. The analogy is of interest since the potential surface in the vicinity of a transition state is usually approximated as a hyperbolic paraboloid, and if the change in the relative energy of the two points is taken to be a linear function of position between the two points, the relevance of the parabola/linear perturbation model can be seen.

The Hammond postulate[4] and the Hughes–Ingold–Shapiro generalization[17] are essentially methods of predicting how the structure of a transition state (and its sensitivity to substituent effects) will change when a new substituent is introduced. Since a nonlinear transition state has $3N - 6$ internal degrees of freedom, a structural change could produce a perturbation in geometry along one or more of them. Hammond's postulate furnishes a prediction regarding the geometry perturbation along one of these degrees of freedom (i.e., the reaction coordinate), and it does so in terms of the relative energies of two structures located in opposite directions along the reaction coordinate (i.e., the reactants and products). If this idea is carried to its logical extreme, in the form of the Hughes–Ingold–Shapiro generalization, geometric distortions along each of the remaining $3N - 5$ coordinates could be predicted in terms of the relative energies of two reference structures located in opposite directions along each internal co-

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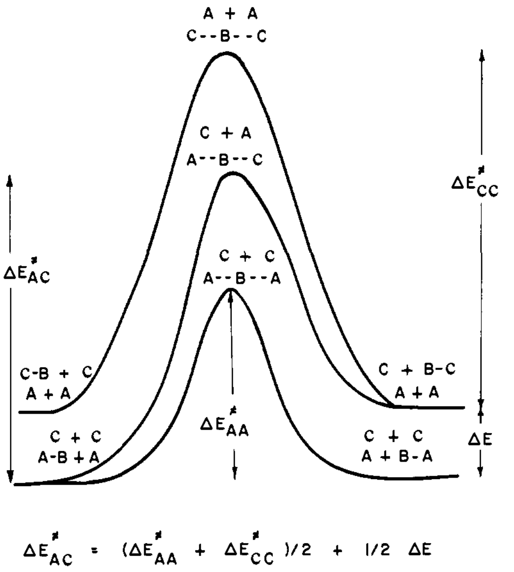

Figure 1. Thermodynamic relationships between reactants, transition states, and products of cross reaction and identity reactions. The barrier to the cross section (A–B + C ⇌ A + B–C) can be expressed in terms of ΔE, $\Delta E^{\ddagger}{}_{AA}$, and $\Delta E^{\ddagger}{}_{CC}$. This relationship can be seen if molecules of A and C are added to the cross reaction and if A + A and C + C are added to the appropriate identity reactions. Alternatively, A–B and C–B can be used for the cross reaction while AB + AB and CB + CB are suitable for the identity reactions.

ordinate. A similar model was formalized by Thornton[14] in 1967 (in terms of the parabola and linear perturbation) and has seen extensive, qualitative use as a two-dimensional version.[14,17-19,33-36]

The Hughes–Ingold–Shapiro generalization allows one to conceptualize separate kinetic and thermodynamic effects on a reaction barrier. Alterations in the energy differences between reactants and products produce geometric distortions in the direction of the reaction coordinate and are associated with a contribution to the change in transition-state energy. Such changes could be termed thermodynamic effects. Distortions perpendicular to the reaction coordinate and the accompanying energy changes are not directly associated with the thermodynamics of the reaction and could be referred to as kinetic effects.

(4) Marcus Rate Theory of Electron Transfer. Marcus' theory[37] for rates of outer-sphere electron-transfer reactions is also relevant to the analysis of kinetic and thermodynamic effects. By assuming that electron transfer proceeds through a transition state with zero (or weak) overlap between the orbitals of the two reactants, Marcus[37] was able to derive the following expression for the dependence of the reaction barrier on $\Delta G°$ for the overall reaction:

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + \tfrac{1}{2}\Delta G° + [(\Delta G°)^2/16\Delta G_0^{\ddagger}] \tag{3}$$

When the reaction is thermoneutral, $\Delta G° = 0$ and the barrier is given by $\Delta G_0^{\ddagger}$, which Marcus' refers to as the intrinsic barrier. For reactions which slightly deviate from thermoneutrality, the barrier also contains a thermodynamic term, $^1/_2\Delta G°$. Consequently, for reactions where $\Delta G° \sim 0$, the barrier can be expressed in terms of a kinetic contribution ($\Delta G_0^{\ddagger}$) and a thermodynamic contribution ($^1/_2\Delta G°$). When $\Delta G° > 0$, a new term becomes important, $(\Delta G°)^2/16\Delta G_0^{\ddagger}$, which contains both thermodynamic and kinetic contributions. In principle, Marcus' equation can treat the same kinetic and thermodynamic effects on *energy* which originate in the HIS generalization[17] and in Thornton's model.[14,17-19,33-36] In fact, it is noteworthy that Marcus' equation can be *derived* from a surface such as the hyperbolic paraboloid envisioned by Hughes, Ingold, and Shapiro.[38d]

(5) The Hemistructural Relationship and Energy Additivity. Recently, a new relationship between geometry and energy in molecules has been discovered.[38] This hemistructural relationship is relevant to the problem of kinetic and thermodynamic control and can be used to show that kinetic and thermodynamic contributions to reaction barriers can be expressed in terms of a simple additivity relationship. Furthermore, it is shown that the kinetic and thermodynamic contributions to a barrier can be evaluated from either experimental data or quantum mechanical calculations.

II. Separation of Kinetic and Thermodynamic Factors

A. Cross Reactions and Identity Reactions. In order to apply the hemistructural relationship[38] to a group transfer reaction, we need to consider the unsymmetrical, or cross,[37] reaction

$$\text{A–B} + \text{C} \rightarrow [\text{A–B–C}]^{\ddagger} \rightarrow \text{A} + \text{B–C} \tag{4}$$

as well as the two symmetrical identity reactions

$$\text{A–B} + \text{A} \rightarrow [\text{A–B–A}]^{\ddagger} \rightarrow \text{A} + \text{B–A} \tag{5}$$

$$\text{C–B} + \text{C} \rightarrow [\text{C–B–C}]^{\ddagger} \rightarrow \text{C} + \text{B–C} \tag{6}$$

The transition state $[\text{A–B–C}]^{\ddagger}$ bears a partial structural resemblance to the reactants and products and to the two identity reaction transition states, $[\text{A–B–A}]^{\ddagger}$ and $[\text{C–B–C}]^{\ddagger}$. Consequently, one might anticipate that the barrier for the cross reaction would show some dependence on the barriers of the two identity reactions as well as on the overall thermodynamics. The quan-

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(38) A structure such as A–B–C is hemistructural to A–B–A and C–B–C if a common origin can be defined so that the nuclear positions of the A–B fragments of A–B–C and A–B–A are superimposable and if the nuclear positions of the B–C fragments of A–B–C and C–B–C are superimposable. A more general definition is given in ref 38a. (a) J. R. Murdoch, *J. Am. Chem. Soc.*, **104**, 588 (1982). (b) J. R. Murdoch and D. E. Magnoli, *J. Am. Chem. Soc.*, **104**, 2782 (1982). (c) It has been shown[38a] that the kinetic energy of a structure could be expressed as

$$T = 2\sum_{\mu}^{\text{occ}}\sum_{i}\sum_{j} C_{i\mu}'\ T_{ij}\ C_{j\mu}' \tag{9a}$$

where $C_{i\mu}'$ and $C_{j\mu}'$ are molecular orbital coefficients and T_{ij} are the kinetic energy matrix elements. It was also pointed out that for proper choice of basis functions, *all* structures could employ the same basis set and the same kinetic energy matrix. Consequently, the change in kinetic energy from one structure to another can be expressed solely in terms of changes in the MO coefficients. For zero-force structures, the virial theorem is applicable so that the total molecular energy (E_T), including nuclear repulsion terms, can be expressed as

$$E_T = -T \tag{9b}$$

The kinetic energy can be evaluated from eq 9a or by summing the diagonal elements of T_0 over the occupied MO's.[49]

$$T_0 = 2(C')^T \cdot T \cdot C' \tag{9c}$$

It is convenient to introduce the eigenvectors (U) of T so that

$$T_0 = 2(C')^T \cdot U \cdot U^T \cdot T \cdot U \cdot U^T \cdot C' \tag{9d}$$

$$T_0 = 2C^T \cdot \Lambda_T' \cdot C \tag{9e}$$

where Λ_T' is the diagonal eigenvalue matrix corresponding to T and $C = U^T C'$. Equation 9e can be used to express the kinetic energy as a quadratic function of the transformed MO coefficients

$$T = 2\sum_{\mu}^{\text{occ}}\sum_{i} C_{i\mu}^2\ \lambda_{ii}' \tag{9f}$$

where $C_{i\mu}$ are elements of C and λ_{ii}' are the eigenvalues of T. Using the virial theorem, the total molecular energy, including nuclear repulsion, can be expressed as

$$E_T = 2\sum_{\mu}^{\text{occ}}\sum_{i} C_{i\mu}^2 \lambda_{ii} \tag{9g}$$

where $\lambda_{ii} = -\lambda_{ii}'$. Equation 9g can be further simplified as

$$E_T = \sum_{i} P_{ii}\lambda_{ii} \tag{9h}$$

(d) J. R. Murdoch, unpublished.

titative nature of this relationship will depend on defining the structural relationships between [A–B–A]‡, [A–B–C]‡, and [C–B–C]‡ and on determining how the similarities in structure relate to the energies of the structures.

B. A New Theory of Nuclear Substitution. In another paper,[38a] the first step in the development of a general theory of nuclear substitution has been presented. The goal of this theory is to describe the changes in wave function, geometry, and molecular properties which accompany the replacement of one molecular fragment by another. Examples of potential applications are the three transition states, corresponding to reactions 4–6, where an "A" fragment is successively replaced by a "C" fragment (viz., [A–B–A]‡, [A–B–C]‡, [C–B–C]‡). The theory is based on analytical SCF equations and, at present, has been carried out to first-order perturbations in MO coefficients and second-order perturbations in energy. Using the Hellmann–Feynman theorem and the successive changes in wave function between [A–B–A]‡, [A–B–C]‡, and [C–B–C]‡,[38a] it can be shown that if the two symmetrical structures occur at saddle points on a potential surface, then the hemistructural geometry[38] of [A–B–C]‡ will also occur at a saddle point, subject to certain limitations.[38a,b] The energy differences between the three transition states can be either additive or nonadditive, but it is significant that neither case requires that the A, B, or C fragments behave as equivalent groups in the three different transition states.[38a,b] The maintenance of constant electronic structure over the corresponding fragments in [A–B–A]‡, [A–B–C]‡, and [C–B–C]‡ is not a prerequisite for observing either energy additivity or the hemistructural relationship.[38]

The relationships mentioned above[38] derive in part from perturbation theory, and it is conceptually useful to start with an unperturbed reference that is structurally as close as possible to the perturbed molecules. A thermodynamic "balancing" trick accomplishes this purpose and is carried out by adding two molecules of B–C to each side of reaction 5, two molecules of A–B to each side of reaction 6, and one molecule each of A–B and B–C to the left and right sides of reaction 4. Note that the *relative* energy of each point on the potential surface for each reaction is unchanged by this procedure.

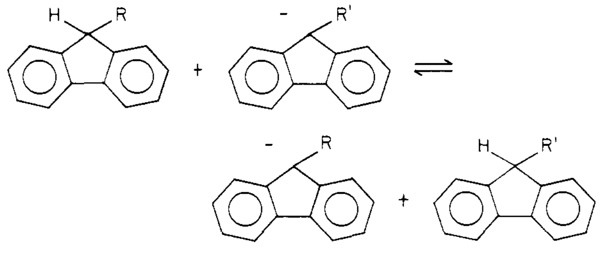
The applicability of perturbation theory is dependent on the degree to which the wave function changes when [A–B–A]‡ is altered to [A–B–C]‡.[38] Using the "balanced" structures, the comparison is between [A–B–A]‡ + C–B + C–B and [A–B–C]‡ + A–B + C–B. This is similar to a comparison between A + C–B + C–B and C + A–B + C–B where the energy difference is ΔE for reaction 4. Consequently, when ΔE is close to zero, it would not be unreasonable to find that the energy difference and changes in wave function between [A–B–A]‡ + C–B + C–B and [A–B–C]‡ + A–B + C–B are also small. As a result, $\Delta E \sim 0$ may be a sufficient condition for the hemistructural relationship to apply to the cross reaction transition state.[39]

C. Identity Reaction Barriers and ΔE. A Limiting Case. A special case of the hemistructural relationship corresponds to energy additivity.[38a] The importance of this can be seen in Figure 1, where the thermodynamic balancing conditions have been added. Note that the reactants for the two identity reactions are spaced at ΔE for the cross reaction and that the energy of the cross reaction transition state is the mean of the energies for the corresponding identity reactions. Using these relationships, an expression for the barrier to the cross reaction can be derived

$$\Delta E^\ddagger = {}^1\!/_2(\Delta E^\ddagger{}_{AA} + \Delta E^\ddagger{}_{CC}) + {}^1\!/_2\Delta E \qquad (7)$$

where $\Delta E^\ddagger{}_{AA}$ and $\Delta E^\ddagger{}_{CC}$ are the two identity barriers and ΔE is the energy change for reaction 4. Given the conditions[38a] leading to the hemistructural relationship and energy additivity for the transition states, eq 7 gives a rigorous[38a] separation of kinetic and thermodynamic contributions to the barrier of the cross reaction. If "C" is varied through a sequence of structures, positive increases in ΔE will produce increases in the barrier but only half as large as in ΔE. Furthermore, $\Delta E^\ddagger{}_{CC}$ can be expected to vary. If the change in $\Delta E^\ddagger{}_{CC}$ is in the same direction as for ΔE, the reaction will appear to be under thermodynamic control, whereas if the change in $\Delta E^\ddagger{}_{CC}$ is in the opposite direction and large enough to offset the change in ΔE, the reaction will appear to be kinetically controlled. Equation 7 gives a reasonable theoretical framework for understanding kinetic and thermodynamic control in terms of substituent effects on the barriers of two identity reactions as well as on the overall thermodynamics. The major significance of eq 7 is that it gives the correct description for a cross reaction barrier when the hemistructural relationship and energy additivity are applicable. Since the conditions known to be necessary for energy additivity are now much less restrictive than formerly believed,[38a] it would not be surprising if eq 7 should give a good account of barriers for real reactions where modest changes in structure are made.

D. Steric Effects and Energy Additivity. (1) Proton Transfer between Substituted Fluorenes and Fluorenyl Anions. One mechanism that could conceivably lead to a breakdown of the hemistructural relationship is the introduction of bulky substituents on the end atoms. It is interesting to note that in the proton-transfer reactions between 9-alkylfluorenes and 9-alkylfluorenyllithium, steric effects appear to be small and their contribution to nonadditivity in the relative barriers to reaction appears to be negligible.[40]



(8)

This is a rather remarkable result considering that the substituents are located on the same carbon involved in the proton transfer and that the substituents involve various combinations of R = H, Me, Et, *i*-Pr, and *t*-Bu. This observation is unprecedented and tentatively suggests that unusually large steric interactions will be necessary to force a breakdown of the hemistructural relationship.

(2) Proton-Bound Dimers in the Gas Phase. The energies of proton-bound dimers of various amines, neutral molecules, and anions have also been shown to exhibit close additivity relationships.[41] For example,[41] the energy of [*sec*-BuNH$_2$·H·NHMe$_2$]$^+$ has been shown to be 0.25 kcal less than the mean energies of the two symmetrical complexes, [*sec*-BuH$_2$N·H·NH$_2$-*sec*-Bu]$^+$ and [Me$_2$HN·H·NHMe$_2$]$^+$. Similar results[41] have been found for about 40 other proton-bound dimers where $\Delta H°$ for the reaction, $R_1NH_3^+ + R_2NH_2 \rightarrow R_1NH_2 + R_2NH_3^+$, is around 0 to 3 kcal/mol. Steric effects on the dimer heat of formation appear negligible, constant or nearly additive.

E. Separation of Kinetic and Thermodynamic Factors Is Rigorous as a Limiting Case. Comparison of eq 7 with eq 3 shows that Marcus' intrinsic barrier, $\Delta G_0^\ddagger$, corresponds to ${}^1\!/_2(\Delta E^\ddagger{}_{AA} + \Delta E^\ddagger{}_{CC})$. Marcus[42] derived this same result from the weak overlap assumption by suggesting that the intrinsic barrier should consist of a separate term for each reactant. These assumptions are

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(39) Strictly speaking, $\Delta E \sim 0$ is a necessary condition. Rigorously, the hemistructural condition will apply as the structures A and C converge, but this may not be necessary. Energy differences between B′–A + B–C and B′–C + B–A will also be small if the B′ and B fragments are similar, particularly when B–C and B–A bond energies are similar. Examination of heats of formation for simple organic compounds (D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969) shows that such energy differences are often within the range of 0–6 kcals. This suggests that the structural changes might be considered as small perturbations (ref 38a) in terms of the total wave functions. This point needs further evaluation.

(40) J. R. Murdoch, J. A. Bryson, D. F. McMillen, and J. I. Brauman, *J. Am. Chem. Soc.*, **104**, 600 (1982).

(41) (a) D. E. Magnoli and J. R. Murdoch, *J. Am. Chem. Soc.*, **103**, 7465 (1981); (b) D. H. Aue and M. T. Bowers, *Gas Phase Ion Chem.*, **8**, 1 (1979).

(42) R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).

appropriate for an outer-sphere electron-transfer reaction which involves little overlap between the reacting orbitals but could be questioned when applied to reactions involving bond cleavage and bond formation.[42,43] Marcus has recognized this limitation[42,43] and has shown[43b] that BEBO, and a more general method of which BEBO is a special case, give eq 7 in the limit of small ΔE and small $|\Delta E^{\ddagger}_{\mathrm{AA}} - \Delta E^{\ddagger}_{\mathrm{CC}}|$. A later empirical derivation[44] of Marcus' equation (eq 3) avoids both the weak overlap approximation as well as the specialized bond energy/bond order (BEBO) assumptions, which seem more appropriate to radical transfer reactions. The present derivation, through an ab initio SCF framework,[38] establishes eq 7 as a correct *limiting* case for all classes of group transfer reactions (including electron transfer) and removes the empirical character of previous derivations.[43b,44,45]

III. Interplay of Kinetic and Thermodynamic Factors

A. Breakdown of the Hemistructural Relationship. One important question dealing with the hemistructural relationship involves the range of ΔE where energy additivity will be observed. Several authors[46-48] have commented on the fact that Bronsted plots are often linear over long regions of $\Delta\mathrm{p}K$ (~10 pK units) and have suggested that substantial substituent effects (13 kcal or more) on ΔG° may not necessarily result in an appreciable shift in transition-state structure. This conclusion is in accord with other results[38a] which have shown that energy additivity and geometry additivity will go hand in hand and that geometry additivity may persist even when energy changes show some nonlinearity.

The long linear regions observed in many Bronsted plots can be interpreted in terms of Marcus' intrinsic barrier, $\Delta G_0^{\ddagger}$. The nonlinearity of $\Delta G^{\ddagger}$ with respect to ΔG° is due to the quadratic term in eq 3 (i.e., $(\Delta G^{\circ})^2/16\Delta G_0^{\ddagger}$), which in turn depends on the relative magnitude of ΔG° and $\Delta G_0^{\ddagger}$ For a fixed value of ΔG°, the nonlinearity will decrease as the intrinsic barrier increases so that linear Bronsted plots over 10-pK units would be expected for intrinsic barriers greater than 15 kcal/mol.

While Marcus' relationship is useful for gaining qualitative insights, the numerical deductions from this theory could easily be questioned. Consequently, it would be instructive to approach the extension of eq 7 from an alternative viewpoint. Two previous options have already been noted.[43b,44]

B. Expressing the Total Energy in Terms of MO Coefficients. It is possible to express the total energy of a molecule as

$$E_{\mathrm{T}} = \sum_i P_{ii}\lambda_{ii} \tag{9}$$

where P_{ii} are the diagonal elements of the transformed density matrix,[38a,c] $U^{\mathrm{T}}\cdot P^0\cdot U$. Since the λ_{ii} are constant,[38,50] eq 9 can be used to express the total molecular energy, including nuclear repulsion, for any zero force structures which are isoelectronic and related to each other by an arbitrary transformation of nuclear coordinates (i.e., isomeric). In particular eq 9 can be used to interrelate the total energies of the reactants, transition state, and products through changes in the transformed density matrix elements. Equation 9 is an important result since P_{ii} can be broken down into contributions from each molecular orbital,[51] thus allowing the total molecular energy, including nuclear repulsion, to be divided into terms associated with particular MO's.

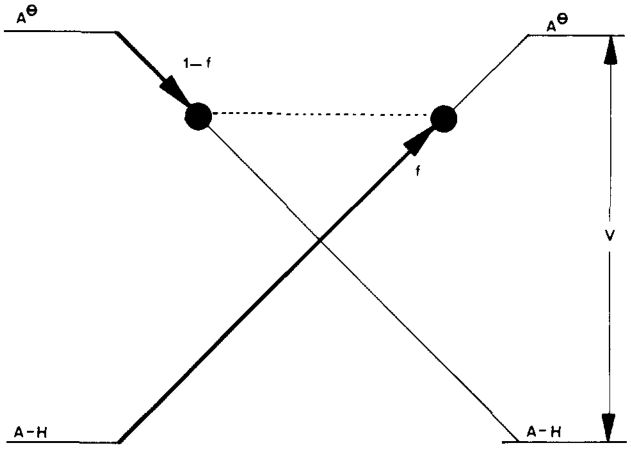

Figure 2. Energetic contributions of two half-reactions to the identity reaction barrier. For $f > {}^1/_2$, the thermodynamic contribution of the uphill half-reaction outweighs the contribution of the downhill half-reaction, and a barrier results. For $f < {}^1/_2$, the intermediate is more stable than either reactant or product.

C. A Special Case—Proton-Transfer Reactions and Intrinsic Barriers. This property is useful for analyzing the energetics of proton-transfer reactions such as

$$\mathrm{A{-}H} + {}^{-}\mathrm{C} \rightleftharpoons \mathrm{A}^{-} + \mathrm{H{-}C} \tag{10}$$

if the overall reaction is divided into two "half"-reactions[52]

$$\mathrm{A{-}H} \rightarrow \mathrm{A}^{-} \qquad V_1 \tag{11}$$

$$^{-}\mathrm{C} \rightarrow \mathrm{H{-}C} \qquad -V_2 \tag{12}$$

Since each acid and its conjugate base are isoelectronic, the number of MO's on the left and right side of each half-reaction is unchanged. Consequently, eq 9 can be divided into two parts so that the total energy of the reactants is expressed as

$$E_{\mathrm{T}}^{\mathrm{r}} = \sum_i P_{ii}^{\mathrm{AH}}\,\lambda_{ii} + \sum_i P_{ii}^{\mathrm{C}}\,\lambda_{ii} \tag{13}$$

$$E_{\mathrm{T}}^{\mathrm{r}} = P_{\mathrm{AH}} + P_{\mathrm{C}} \tag{13a}$$

where P_{ii}^{AH} represents the transformed density matrix elements for A–H and P_{ii}^{C} are the corresponding quantities for C^-. We can gain some insight into the nature of the barrier to proton transfer by considering that the P_{ii}'s will start with values characteristic of the reactants and end with values appropriate to the products. From eq 11 and 12 it can be seen that P_{AH} will increase on going from reactants to products, while P_{C} will decrease. The barrier for the overall reaction is given by

$$\Delta E^{\ddagger} = (P^{\ddagger}_{\mathrm{AH}} - P_{\mathrm{AH}}) + (P^{\ddagger}_{\mathrm{C}} - \mathrm{P_C}) \tag{14}$$

while ΔE is given by

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(43) (a) R. A. Marcus, *Faraday Symp. Chem. Soc.*, **10**, 60 (1975); (b) *J. Phys. Chem.*, **72**, 891 (1968).

(44) J. R. Murdoch, *J. Am. Chem. Soc.*, **94**, 4410 (1972).

(45) M. A. Ratner and R. D. Levine [*J. Am. Chem. Soc.*, **102**, 4898 (1980)] have correctly recognized that eq 7 can be obtained by assuming that (a) the activation process for each chemical species is independent of its reacting partner and (b) the structures of the various fragments are the same in the identity and cross reactions. While these assumptions are sufficient for energy additivity, the results on the hemistructural relationship[38] show that these conditions are not necessary in order for eq 7 to hold. As a point of historical interest, it is worth noting that Marcus obtained eq 7 by using assumption a.[42] By applying assumption a to the derivative, $\partial\Delta G^{\ddagger}/\partial\Delta G^{\circ}$, it is possible to derive the entire Marcus relationship (eq 3) which includes eq 7 as a special case.[44] The correlation of eq 7 with energy additivity has been used to interpret the relationship between experimental identity and cross reactions for a proton-transfer process.[40]

(46) D. S. Kemp and M. L. Casey, *J. Am. Chem. Soc.*, **95**, 6670 (1973).

(47) A. Streitwieser, Jr., W. B. Hollyhead, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *J. Am. Chem. Soc.*, **93**, 5088 (1971).

(48) F. G. Bordwell and W. J. Boyle, Jr., *J. Am. Chem. Soc.*, **93**, 511, 512 (1971).

(49) For convenience, the basis set is taken to be orthogonal.

(50) When the MO's of the reactants which have been labeled as occupied remain occupied for the transition state and the products, the changes in C_{ii} are continuous. The λ_{ii} are independent of the MO coefficients and the particular structure.

(51) The density matrix element, P_{kl} is equal to $2\sum_{\mu}^{\mathrm{occ}} a_{\mu k}a_{\mu l}$, where $a_{\mu k}$ are the MO coefficients.[38] The transformed density matrix $U^{\mathrm{T}}\cdot P\cdot U$ is equivalent to $U^{\mathrm{T}}\cdot\sum_{\mu}^{\mathrm{occ}} A_{\mu}\mathrm{U}$ and $\sum_{\mu}^{\mathrm{occ}} U^{\mathrm{T}}A_{\mu}\cdot U$ where $\sum_{\mu}^{\mathrm{occ}} A_{\mu} = P$. The present finding that specific interaction terms are not required has other precedents. For example, P. Politzer and R. G. Parr have shown that molecular energies can be written as a sum of atomic-like terms, with no other contributions [*J. Chem. Phys.*, **61**, 4258 (1974)]. However, this approach differs considerably from the present one in that Politzer and Parr divide the nuclear repulsion interactions between the respective nuclei. On the other hand, eq 9a shows that the kinetic energy can be expressed without interaction terms, and at stationary points, eq 9b is applicable so that the total energy can also be expressed without interaction terms.

(52) Note that the two "half"-reactions do not balance with respect to mass individually but that the sum does. Also note that the missing fragment (H^+) has no electronic energy.

$$\Delta E = (P_A - P_{AH}) + (P_{CH} - P_C) \qquad 14a)$$

It is apparent that if P_{AH} and P_C change to the same fractional extent (f) at the transition state, then no barrier or minimum is possible unless $f < 0$ or $f > 1$. When $P^{\ddagger}_{AH}$ and $P^{\ddagger}_C$ are intermediate with respect to the initial values (P_{AH} and P_C) and final values (P_A and P_{CH}), an energy maximum or minimum separating the reactants or products requires that the extent of fractional change be different for $P^{\ddagger}_{AH}$ and $P^{\ddagger}_C$. This is illustrated for an identity reaction in Figure 2 where the two half-reactions are indicated by the diagonal arrows. For $f = {}^1/_2$, the increase in P_{AH} is exactly offset by the decrease in P_A so that the "transition state" occurs at the same energy as the reactants and products. When $f < {}^1/_2$ then an energy minimum and a stable intermediate are produced. Using eq 13, 13a, and the relationships in figure 2, the barrier for the identity reaction can be expressed in terms of f and V.

$$\text{A-H} + {}^-\text{A} \rightleftharpoons \text{A}^- + \text{H-A} \qquad (15)$$

$$\Delta E^{\ddagger}_{AA} = f^0_A V_A - (1 - f^0_A)V_A = (2f^0_A - 1)V_A = (P^{0\ddagger}_{AH} - P_{AH}) + (P^{0\ddagger}_A - P_A) \qquad (16)$$

$$f^0_A = (\Delta E^{\ddagger}_{AA} + V_A)/2V_A \qquad (17)$$

These relationships can be used to demonstrate a very interesting property of f^0_A and f^0_C when the hemistructural relationship applies to the transition state of the cross reaction (A-H + C$^-$ $\rightleftharpoons$ A$^-$ + HC; eq 10). Given the hemistructural relationship, eq 7 can be applied to reaction 10 and rewritten as

$$\Delta E^{\ddagger} = \frac{(f^0_A - 1/2)\Delta E^{\ddagger}_{AA}}{(2f^0_A - 1)} + \frac{(f^0_C - 1/2)\Delta E^{\ddagger}_{CC}}{(2f^0_C - 1)} + {}^1\!/_2\Delta E \qquad (18)$$

and by using eq 16, the relationship $\Delta E = V_A - V_C$ and eq 14, it can be shown that

$$\Delta E^{\ddagger} = f^0_A V_A - (1 - f^0_C)V_C = (P^{0\ddagger}_{AH} - P_{AH}) + (P^{0\ddagger}_C - P_C) \qquad (19)$$

By comparing eq 19 and 11 it is apparent that the terms characterizing the energy change in each reactant [i.e., $(P^{0\ddagger}_{AH} - P_{AH})$ and $(P^{0\ddagger}_C - P_C)$] are effectively transferable from the identity reactions to the cross reactions.[61]

The hemistructural relationship and the finding that the total energies of the reactants, products, and transition state can be expressed in the remarkably simple form of eq 13a have given us some new insights into the nature of barriers to proton transfer. In particular, we have seen that the identity barrier should be proportional to the proton affinity of the base (eq 16) and that this proportionality should carry over into the cross reaction transition state (eq 19). Consequently, the barrier of a cross reaction should depend on the proton affinities of the bases in two ways: once as a simple difference in the ${}^1/_2\Delta E$ term and once as a contribution to the intrinsic barrier. Since the proton affinities affect both ΔE and $\Delta E^{\ddagger}_0$, it seems unlikely that intrinsic barriers will always be independent of ΔE (or $\Delta G°$).[16,44,53] This has been confirmed experimentally in at least two instances.[40,41]

Equations 7, 16, and 19 have been obtained on a relatively sound[38a] theoretical basis. To go beyond the hemistructural relationship, it is necessary to determine how the transformed density matrix elements (eq 13) vary with changes in nuclear position. The basic theoretical framework for this has been laid down,[38a] but certain refinements remain to be completed. Rather than wait for this result, we shall temporarily leave the warm nest of rigor and venture out onto the thin ice of empiricism.

D. An Empirical View on the Breakdown of the Hemistructural Relation. The basic form of eq 13, as well as chemical intuition,[4,5,7,14,17-37] suggests that the extreme limits of transition state structure will lie at the reactants for very exergonic reactions and at the products for very endergonic reactions. Equation 14 demonstrates that no new terms must be added to eq 19, but the modifications to eq 19 must include some mechanism for transforming f^0_A and $(1 - f^0_C)$ to zero for one case and unity for the other.

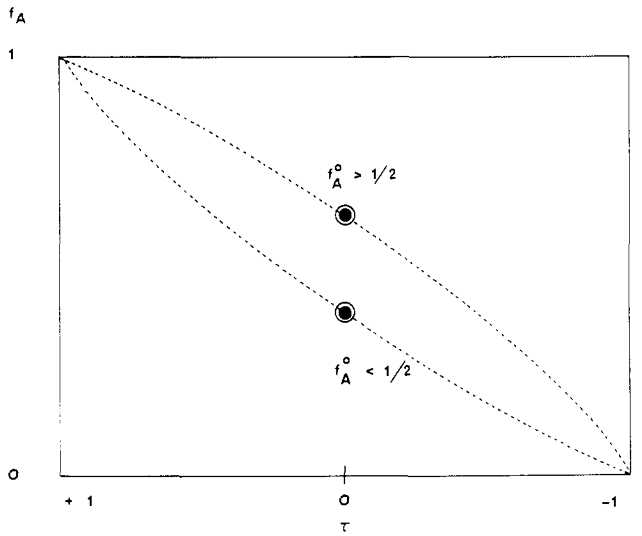

Figure 3. Variation of f_A with τ. The parameter f^0_A represents the fraction to which the thermodynamic contribution of the uphill half-reaction appears at the transition state of the identity reaction. f_A should approach 1 for strongly endothermic reactions and should approach 0 for strongly exothermic reactions. The figure shows a parabolic dependence f_A on the exo/endo thermicity parameter, τ.

At this point it is appropriate to introduce the assumption that f_A and $(1 - f_C)$ can be expressed as functions of a single variable (e.g., τ). The variable τ is expected to exhibit a dependence on ΔE and possibly other parameters such as $\Delta E^{\ddagger}_0$, force constants, or equilibrium bond lengths. It is convenient to set $\tau = 0$ for $\Delta E = 0$ and $\tau = \pm 1$ for ΔE corresponding to the respective endothermic and exothermic limits (finite or $\pm\infty$). The correspondence between τ and f_A and $(1 - f_C)$ is assumed for two values ($\tau = -1$, $f_A = (1 - f_C) = 0$; $\tau = +1$, $f_A = (1 - f_C) = 1$) and is known for a third [$\tau = 0$, $f_A = f^0_A$ and $(1 - f_C) = (1 - f^0_C)$]. These relationships are illustrated in Figure 3.

Given the above assumption that f_A is dependent on a single variable, τ, we can write the following general expression for f_A,

$$f_A = f^0_A + {}^1\!/_2 g_1(\tau) + [(1 - 2f^0_A)/2]g_2(\tau) \qquad (20)$$

where $g_1(\tau)$ and $g_2(\tau)$ are odd and even functions of τ,[54] respectively. Without loss of generality; $g_1(\tau) = g_2(\tau) = 1$ for $\tau = 1$; $g_1(\tau) = g_2(\tau) = 0$ for $\tau = 0$; $-g_1(\tau) = g_2(\tau) = 1$ for $\tau = -1$. Introducing the third assumption that f_C can also be expressed in terms of $g_1(\tau)$ and $g_2(\tau)$,

$$(1 - f_C) = (1 - f^0_C) + {}^1\!/_2 g_1(\tau) + [(2f^0_C - 1)/2]g_2(\tau) \qquad (21)$$

Substituting f_A and $(1 - f_C)$ for f^0_A and $(1 - f^0_C)$ in eq 19,

$$\Delta E^{\ddagger} = V_A[f^0_A + {}^1\!/_2 g_1(\tau) + [(1 - 2f^0_A)/2]g_2(\tau)] - V_C[(1 - f^0_C) + {}^1\!/_2 g_1(\tau) + [(2f^0_C - 1)/2]g_2(\tau)] \qquad (22)$$

After substituting eq 16 and 19 and rearranging,

$$\Delta E^{\ddagger} = [1 - g_2(\tau)]\Delta E^{\ddagger}_0 + [1 + g_1(\tau)]{}^1\!/_2\Delta E \qquad (23)$$

For $\tau = 0$, $g_2(\tau) = g_1(\tau) = 0$, and eq 23 reduces to the hemistructural limit, eq 7. For monotonic $g_2(\tau)$ and $g_1(\tau)$, increases in τ reduce the contribution of the intrinsic barrier to $\Delta E^{\ddagger}$, while the importance of ΔE increases until $\Delta E^{\ddagger} = \Delta E$ at $\tau = 1$. As τ becomes progressively more negative, both ΔE and $\Delta E^{\ddagger}_0$ contribute less to $\Delta E^{\ddagger}$, which converges to zero for $\tau = -1$. Equation 23 provides a reasonable basis for understanding the changes in the relative importance of kinetic and thermodynamic contributions

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(53) E.g., M. M. Kreevoy and Sea-Wha Oh, *J. Am. Chem. Soc.*, 95, 4805 (1973).

(54) An odd function of τ can be expressed solely in terms of odd power monomials. An even function of τ can be expressed solely in terms of even power monomials.

Table I. Comparison of τ and $\Delta E^{\ddagger}/\Delta E_0^{\ddagger}$ –Marcus vs. Sigmoidal Theories, $\epsilon = 1$

$\Delta E/$	τ				δ^a		
$\Delta E_0^{\ddagger}$	Marcus	sin	arctan	tanh	δ_{sin}	δ_{arctan}	δ_{tanh}
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	0.125	0.25	0.24	0.24	0.02	0.01	0.01
1.00	0.25	0.48	0.42	0.46	0.05	0.03	0.05
2.00	0.50	0.84	0.64	0.76	0.12	0.02	0.07
3.00	0.75	0.99	0.74	0.91	0.06	0.00	0.02
π	0.78	1.00	0.75	0.92	0.05	0.00	0.02
3.50	0.875	1.00	0.78	0.94	0.02^b	0.01	0.00
4.00	1.00	1.00	0.80	0.96	0.00^b	0.00^b	0.00^b

[a] $\delta = (\tau_{\text{Marcus}} - \tau_{\text{sigmoidal}})^2 = (\Delta E^{\ddagger}/\Delta E_0^{\ddagger})_{\text{Marcus}} - (\Delta E^{\ddagger}/\Delta E_0^{\ddagger})_{\text{sigmoidal}}$; |Marcus barrier| $\geqslant$ |signoidal barrier| for $\tau_{\text{sigmoidal}} \geqslant \tau_{\text{Marcus}}$. [b] Equation 24 requires that $|\Delta E| \leqslant 2(1+\tau)|\Delta E_0^{\ddagger}|$. For ΔE outside this range, eq 24 is replaced by $\Delta E^{\ddagger} = \Delta E$ for positive $\Delta E^{\ddagger} = 0$ for negative ΔE. See footnote 55.

to $\Delta E^{\ddagger}$ as ΔE departs from zero and approaches the endothermic and exothermic limits.

The simplest odd and even functions of τ are the monomials, τ and τ^2. Substituting $\tau = g_1(\tau)$ and $\tau^2 = g_2(\tau)$ into eq 23,

$$\Delta E^{\ddagger} = (1 - \tau^2)\Delta E_0^{\ddagger} + (1 + \tau)\tfrac{1}{2}\Delta E \tag{24}$$

It is interesting to note that for $\tau > 0$ and $\Delta E_0^{\ddagger}$, $\Delta E > 0$, $\Delta E^{\ddagger}$ converges to ΔE from above, provided that $\Delta E \leq 4\Delta E_0^{\ddagger}$.[55] This inequality also appears in Marcus' theory, and if τ is set equal to $\Delta E/4\Delta E_0^{\ddagger}$ and substituted into eq 24, Marcus' equation is produced. However, this choice for τ is not the only possibility.

Table II. Energies of Rare Gas Atoms and Derivatives

	energy, hartree		
	X = He	X = Ne	X = Ar
X	−2.807784	−126.604525	−521.222881
X^+H	−2.854369	−126.794722	−521.383544
XH^+X	−5.685524	−253.484377	−1042.651723
HeH^+X		−129.607952	−524.192671
NeH^+X			−648.067884

Table III. Geometries of Protonated Rare Gas Atoms and Derivatives

	X		
	He	Ne	Ar
r_{XH}, Å	0.9301	0.9867	1.3482
r_{HeHX},[a] Å	1.0220	1.0120	1.3562
r_{NeHX}, Å	1.2185	1.0929	1.5266
r_{ArHX}, Å	1.3593	1.0889	1.5155

[a] r_{HeHX} = H–X bond length in HeH^+X.

Table IV. Intrinsic Barriers of the Identity Reactions

	HeH^+He	NeH^+Ne	ArH^+Ar
$\Delta E_0^{\ddagger}$, kcal	−14.66	−53.42	−28.42
V	29.23	119.35	100.82
f^0	0.2493	0.2762	0.3590

The form of eq 24 places certain restrictions on τ since there are constraints on the behavior of $\Delta E^{\ddagger}$ as the limiting cases are reached. For example, the first derivative of eq 24 with respect to ΔE might approach unity or vanish as $\Delta E^{\ddagger} \rightarrow \Delta E$ or $\Delta E^{\ddagger} \rightarrow 0$. These considerations[56,57] suggest a sigmoidal dependence of

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(55) This can be shown by setting $\tau = \pm(1 - \epsilon)$ for $\epsilon \sim 0$, substituting into eq 24, dropping ϵ^2 terms, and comparing $\Delta E^{\ddagger}$ with the rhs. For $\tau > 0$, $\Delta E_0^{\ddagger}$, $\Delta E < 0$, $\Delta E^{\ddagger}$ approaches ΔE from below for $\Delta E \geq 4\Delta E_0^{\ddagger}$, For $\tau < 0$, $\Delta E_0^{\ddagger} < 0$, $\Delta E > 0$, $\Delta E^{\ddagger}$ approaches zero from below for $4|\Delta E_0^{\ddagger}| \geq \Delta E$. For $\tau < 0$, $\Delta E_0^{\ddagger} > 0$, $\Delta E < 0$, $\Delta E^{\ddagger}$ approaches zero from above for $4\Delta E_0^{\ddagger} \geq |\Delta E|$. Since ϵ^2 terms are omitted in the above derivation, the inequalities (e.g., $\Delta E \leq 4\Delta E_0^{\ddagger}$) are strictly valid only in the limit $\epsilon \rightarrow 0$, which is equivalent to $|\tau| \rightarrow 1$ as $|\Delta E| \rightarrow 4|E_0^{\ddagger}|$. If $|\tau| \rightarrow b < 1$ as $|\Delta E| \rightarrow 4|\Delta E_0^{\ddagger}|$, then the factor of 4 in the above inequalities is reduced somewhat, and ΔE is confined to the range $-(4 - 2\epsilon)|\Delta E_0^{\ddagger}| \leq \Delta E \leq (4 - 2\epsilon)|\Delta E_0^{\ddagger}|$. The fact that inequalities of this type often lead to unrealistic behavior at extreme values of ΔE has troubled some authors (e.g., ref 27). Marcus has avoided these difficulties by using eq 3 for $|\Delta G°| \leq 4|\Delta G_0^{\ddagger}$ and setting $\Delta G^{\ddagger} = \Delta G°$ for $|\Delta G°| > 4|\Delta G_0^{\ddagger}$. This procedure eliminates the above problems, but introduces two new features: (1) the barrier of a highly endergonic reaction approaches $\Delta G°$ for a *finite* value of $\Delta G°$; (2) $\Delta G°$ is a continuous function of $\Delta G°$, but the derivative, $(\partial\Delta G^{\ddagger}/\partial\Delta G°)_{\Delta G_0^{\ddagger}}$ is discontinuous at $|\Delta G°| = 4|\Delta G_0^{\ddagger}|$. Some authors[27] have suggested that it would be "more rigorous" if the endergonic and exergonic limits for the barrier are reached only as $\Delta G° \rightarrow \pm\infty$ and if the derivative $\partial\Delta G^{\ddagger}/\partial\Delta G°)_{\Delta G_0^{\ddagger}}$ is continuous for all values of $\Delta G°$. In practice, no large differences have been noted between Marcus' barriers and the barriers of these "more rigorous" methods (e.g., ref 27 and 43b). The present authors take a neutral stand on this question for the moment and simply note that it has not yet been theoretically established whether approximations beyond eq 7 can still be expressed in terms of simple parameters such as $\Delta G_0^{\ddagger}$ and $\Delta G°$. Basing a derivation on empirical approximations which differ from those of Marcus may yield an exergonic limit for a barrier at $\Delta G° = -\infty$ and may avoid discontinuous derivatives, but there is no guarantee that the calculated barriers will be an improvement over the corresponding Marcus barriers. In any event, the range where ΔE results in a barrier can be extended indefinitely by choosing alternative odd or even functions of τ in eq 23. For example, if τ^2 in eq 24 is replaced by τ^{2n}, the endothermic limit for ΔE increases from $4\Delta E_0^{\ddagger}$ to $4n\Delta E_0^{\ddagger}$. Equation 23 is consistent with either a finite or infinite endothermic limit for ΔE: using simple algebra, it can be shown that if

$$\lim_{\tau \rightarrow 1}\left[\frac{1 - g_2(\tau)}{1 - g_1(\tau)}\right]$$

is finite (infinite) then $\Delta E^{\ddagger} \rightarrow \Delta E$ from above for a finite (infinite) value of $\Delta E > 0$. Two examples of $g_1(\tau)$ and $g_2(\tau)$ which correspond to infinite endothermic limits are $g_1(\tau) = {}^3/_2\tau - {}^1/_2\tau^3$; $g_2(\tau) = \tau^2$ and $g_1(\tau) = \sin(\pi\tau/2)$; $g_2(\tau) = 1 - \cos(\pi\tau/2)$. In deriving eq 23, it has been assumed that f_A and $(1 - f_C)$ can be described in terms of the same parametric functions, $g_1(\tau)$ and $g_2(\tau)$. If this restriction is relaxed so that f_A and $(1 - f_C)$ use different parametric functions [e.g., $g_1{}^A(\tau)$, $g_2{}^A(\tau)$, $g_1{}^C(\tau)$, $g_2{}^C(\tau)$], then eq 23 assumes the form

$$\Delta E^{\ddagger} = [\Delta E^{\ddagger}{}_0 + V_A(\tfrac{1}{2} - f^0{}_A)g_2{}^A(\tau) + V_C(\tfrac{1}{2} - f_C{}^0)g_2{}^C(\tau)] + \tfrac{1}{2}[\Delta E + V_A g_1{}^A(\tau) - V_C g_1{}^C(\tau)] \tag{23a}$$

Note that the kinetic term contains a weighted *sum* of V_A and V_C, while the thermodynamic term contains a weighted *difference* of V_A and V_C.

(56) It can be shown that acceptable limits for the derivatives of τ are as

$$0 = \left(\frac{d\tau}{d\Delta E}\right)_{\tau=1} = \left(\frac{d\tau}{d\Delta E}\right)_{\tau=-1} = \left(\frac{d^2\tau}{d\Delta E^2}\right)_{\tau=1} = \left(\frac{d^2\tau}{d\Delta E^2}\right)_{\tau=-1}$$

follows:[57]

$$\frac{1}{2\Delta E_0^{\ddagger}} \geq \left(\frac{d\tau}{d\Delta E}\right)_{\tau=0} \geq \frac{1}{4\Delta E_0^{\ddagger}}$$

The limit on $(d\tau/d\Delta E)_{\tau=0}$ is noteworthy since the lower limit is identical for that when $\tau = \Delta E/4\Delta E_0^{\ddagger}$, which leads to the Marcus relationship. For simplicity, these derivatives are partial derivatives where V_C, f_A, f_C are constant or V_A, f_A, f_C are constant. These solutions are not unique if ${}^1/_2\Delta E - 2\tau\Delta E_0^{\ddagger}$ approaches zero as occurs for $\tau = \Delta E/4\Delta E_0^{\ddagger}$ in Marcus' theory.

(57) Differentiating eq 24 with respect to ΔE,

$$\frac{d\Delta E^{\ddagger}}{d\Delta E} = \frac{d\Delta E_0^{\ddagger}}{d\Delta E}(1 - \tau^2) + \tfrac{1}{2}(1 + \tau) + \frac{d\tau}{d\Delta E}[\tfrac{1}{2}\Delta E - 2\tau\Delta E_0^{\ddagger}] \tag{24a}$$

For $\tau = 1$, $d\Delta E^{\ddagger}/d\Delta E$ approaches 1 so that an acceptable solution for $(d\tau/d\Delta E)_{\tau=1}$ is zero. When $\tau = -1$, $d\Delta E^{\ddagger}/d\Delta E$ approaches zero and $(d\tau/d\Delta E)_{\tau=-1} = 0$ is again acceptable. Differentiating again with respect to ΔE

$$\frac{d^2\Delta E^{\ddagger}}{d(\Delta E)^2} = \frac{d\tau}{d\Delta E}\left[1 - 4\tau\frac{d\Delta E_0^{\ddagger}}{d\Delta E}\right] + \frac{d^2\tau}{d(\Delta E)^2}[\tfrac{1}{2}\Delta E - 2\tau\Delta E_0^{\ddagger}] + \frac{d^2\Delta E_0^{\ddagger}}{d(\Delta E)^2}(1 - \tau^2) - 2\Delta E_0^{\ddagger}\left(\frac{d\tau}{d\Delta E}\right)^2 \tag{24b}$$

For $\tau = \pm 1$, $d^2\Delta E^{\ddagger}/d(\Delta E)^2 = 0$, and $d^2\Delta E_0^{\ddagger}/d(\Delta E)^2$ is always zero[56] so that $d^2\tau/d(\Delta E)^2 = 0$ is an acceptable solution. For $\tau = \Delta E = 0$, eq 24b becomes

$$\left(\frac{d^2\Delta E^{\ddagger}}{d(\Delta E)^2}\right)_{\tau=0} = \left(\frac{d\tau}{d\Delta E}\right)_{\tau=0} - 2\Delta E_0^{\ddagger}\left(\frac{d\tau}{d\Delta E}\right)^2_{\tau=0} = \left(\frac{d\alpha}{d\Delta E}\right)_{\tau=0} \tag{24c}$$

The parameter α is equivalent to the Bronsted slope and solving eq 24c for $(d\tau/d\Delta E)_{\tau=0}$

$$\left(\frac{d\tau}{d\Delta E}\right)_{\tau=0} = \frac{1}{2\Delta E_0^{\ddagger}} \text{ or } 0 \text{ for } \frac{d\alpha}{d\Delta E} \ll \frac{1}{8\Delta E_0^{\ddagger}} \tag{24d}$$

$$\left(\frac{d\tau}{d\Delta E}\right)_{\tau=0} = \frac{1}{4\Delta E_0^{\ddagger}} \text{ for } \frac{d\alpha}{d\Delta E} = \frac{1}{8\Delta E_0^{\ddagger}} \tag{24e}$$

Two acceptable solutions for $(d\tau/d\Delta E)_{\tau=0}$ are

$$\frac{1}{2\Delta E_0^{\ddagger}} \geq \left(\frac{d\tau}{d\Delta E}\right)_{\tau=0} \geq \frac{1}{4\Delta E_0^{\ddagger}} \text{ or } \frac{1}{4\Delta E_0^{\ddagger}} \geq \left(\frac{d\tau}{d\Delta E}\right)_{\tau=0} \geq 0 \tag{24f}$$

τ on ΔE.[58,59] Several possibilities include

$$\tau = \sin\,(\Delta E/2\epsilon\Delta E_0^{\ddagger}) \qquad |\Delta E/\Delta E_0^{\ddagger}| \leq \epsilon\pi \tag{25}$$

$$\tau = (2/\pi)\arctan\,(\pi\Delta E/4\epsilon\Delta E_0^{\ddagger}) \tag{26}$$

$$\tau = \tanh\,(\Delta E/2\epsilon\Delta E_0^{\ddagger}) \tag{27}$$

The parameter ϵ has been introduced to give the appropriate limiting slope at $\Delta E = 0$. When $\epsilon = 1$ the slope reaches the upper limit,[57] $^1/_2\Delta E_0^{\ddagger}$, and for $\epsilon = 2$, the slope approaches the Marcus limit, $^1/_4\Delta E_0^{\ddagger}$.[57] These functions for τ can be individually substituted into eq 24 and used to calculate $\Delta E^{\ddagger}$. In Table I, τ is calculated by using eq 25–27. The results are compared with the linear approximation $\tau = \Delta E/4\Delta E_0^{\ddagger}$ and used to compute $\Delta E^{\ddagger}/\Delta E_0^{\ddagger}$ for the various choices of τ. For $\Delta E_0^{\ddagger} = 10$ kcal, the maximum discrepancy in $\Delta E^{\ddagger}/\Delta E_0^{\ddagger}$ between Marcus theory and the "sigmoidal" theories is slightly over 1 kcal.[60] The average difference over the range $0 \leq \Delta E/\Delta E_0^{\ddagger} \leq 4$ amounts to about 0.25 kcal.[60] The significant point is that there is little difference in the barrier predictions between Marcus' theory and the "sigmoidal" theories as a group and an even smaller difference between the "sigmoidal" theories themselves. Marcus has made a similar point in connection with the BEBO extension of the weak overlap electron-transfer theory (eq 3).[43b]

When the slope of the sigmoid functions is adjusted ($\epsilon = 2$) to correspond to the Marcus slope ($^1/_4\Delta E_0^{\ddagger}$), there is no significant difference between any of the theories over the range $0 \leq \Delta E/\Delta E_0^{\ddagger} \leq 3$. At the extreme values of ΔE, the discrepancies range from about 0.25–1.3 kcal for $\Delta E_0^{\ddagger} = 10$ kcal.[60]

E. Summary—Theory vs. Empiricism. The model described above incorporates sound theoretical principles with three empirical assumptions. An important finding is that the energy at the transition state(s) of the A–H–C potential surface can be expressed as the sum of two terms. These terms, respectively, reduce to the total energy of AH and C at the reactants and to the total energy of A and HC at the products. In the hemistructural limit, each term is effectively[61] transferable from one of the two identity reactions. *Consequently, at the transition state, no separate interaction terms between the A and C fragments are specifically required.* It is shown that each of the two terms can be associated with an individual half-reaction. The energy contribution of the "uphill" half-reaction is characterized by a parameter, f_A, while the contribution of the "downhill" half-reaction is measured by $1 - f_C$. The first empirical assumption is that f_A and $1 - f_C$ approach limiting values (0 or 1) for extreme values of $|\Delta E|$. The remaining two empirical assumptions are that f_A and f_C are dependent on a single variable (τ) and that f_A and f_C are expressable as parametric functions of $g_1(\tau)$ and $g_2(\tau)$. This parametric dependence of f_A and $1 - f_C$ on τ is an implicit mechanism for treating transition-state interactions, including those between the A and C fragments. Marcus' equation is a particularly simple, specific case of the general barrier expression (eq 23) for which $g_1(\tau) = \tau$, $g_2(\tau) = \tau^2$, and $\tau = \Delta E/4\Delta E_0^{\ddagger}$. Marcus' equation is an example of a barrier function where $\Delta E^{\ddagger} \rightarrow \Delta E$ from above for a *finite* value of ΔE ($\Delta E^{\ddagger} = \Delta E$ for $\Delta E = 4\Delta E_0^{\ddagger}$). This feature has been criticized[27] and has also been the object of experimental search.[62] It should be noted that whether $\Delta E^{\ddagger} \rightarrow \Delta E$ for finite or infinite values of ΔE depends on the properties of $g_1(\tau)$ and $g_2(\tau)$.[55]

Table V. Barriers of Cross Reactions

	HeH^+Ne	HeH^+Ar	NeH^+Ar
ΔE, kcal	−90.12	−71.58	18.53
$\Delta E_0^{\ddagger}$, kcal	−34.04	−21.54	−40.92
$\Delta E^{\ddagger}$, kcal	−93.53	−72.43	−31.55
$\Delta E^{\ddagger}{}_{\text{Marcus}}$, kcal	−94.01	−72.19	−32.18
$\Delta E^{\ddagger}{}_{\sin}$,[a] kcal	−90.79	−71.60	−31.67
$\Delta E^{\ddagger}{}_{\arctan}$,[a] kcal	−93.91	−72.10	−31.73
$\Delta E^{\ddagger}{}_{\tanh}$,[a] kcal	−92.57	−71.98	−31.69

[a] $\epsilon = 1$.

IV. A Quantum Mechanical Test

A convenient reaction to use as a test case involves proton transfer between rare gas atoms.

$$\text{He–H}^+ + \text{Ne} \rightleftharpoons \text{He} + \text{H–Ne}^+ \tag{28}$$

$$\text{He–H}^+ + \text{Ar} \rightleftharpoons \text{He} + \text{H–Ar}^+ \tag{29}$$

$$\text{Ne–H}^+ + \text{Ar} \rightleftharpoons \text{Ne} + \text{H–Ar}^+ \tag{30}$$

The energies of these structures as well as the intermediate "transition states" were calculated by using GAUSSIAN 70[63] and PROMETHEUS X.[64] Pople's 3G basis set[63] was used and all geometries have been fully optimized to within 5 μhartree of the estimated minimum.[65] The calculated energies and geometries are summarized in Tables II and III.[66]

In table IV, the intrinsic barriers are listed for the three identity reactions. Note that the barriers are negative and are not constant and vary due to changes in both V and f^0. In Table V the barriers for the three cross reactions are reported. Again, note that the intrinsic barriers are not constant and Marcus' equation as well as the three sigmoid "theories" give excellent agreement with the SCF MO barriers. The behavior of the arctan model is particularly striking, showing agreement with the SCF result to within 0.4 kcal over the 108-kcal variation in ΔE!

It is also worth noting that the geometry changes are in good qualitative agreement with the Hughes–Ingold–Shapiro generalization[17] and with Johnston's proposal of bond order conservation. The proton shifts toward the more basic atom, and the degree of the shift increases with the difference[67] in basicity. The geometry of NeH^+Ar is also within 0.004–0.01 Å of the hemistructural

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[58] The limits derived in ref 56 are consistent with a sigmoidal function with an odd number of inflection points.

[59] Marcus has also considered sigmoidal relationships between a perturbational parameter and ΔE. See ref 43b.

[60] This error is proportional to $\Delta E_0^{\ddagger}$.

[61] This does not require that the f^0 terms actually transfer, only that the final result is the same as if they do.

[62] (a) V. Breyman, H. Dreeskamp, E. Koch, and M. Zander, *Chem. Phys. Lett.*, **59**, 68 (1978); (b) M. T. Indelli and F. Scandola, *J. Am. Chem. Soc.*, **100**, 7732 (1978).

[63] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, *QCPE*, **11**, 236 (1973).

[64] PROMETHEUS X is an experimental SCF MO program now under development at UCLA. It will be described in detail elsewhere.

[65] This degree of optimization was carried out since the energy relationships between the structures are not particularly simple unless the structures are zero-force structures.[38a] The quality of these wave functions at the 3-G level is relatively poor and is nowhere close to the HF limit with respect to energy. The wave functions do not satisfy either the virial or Hellmann–Feynman theorems. However, it was found that geometry optimization is sufficient for the total energy to behave as if the virial theorem holds, since scaling to satisfy the virial theorem scarcely changes E_T and has little effect on the relative energy. These points are being pursued but do not materially affect the present conclusions.

[66] It is also relevant to point out that the MO's for the XH^+X-type species are sufficiently localized to make spatial correlations with the MO's for X and H^+X. All of the XH^+X MO's were found to be intermediate in orbital energy relative to the corresponding MO's of X and H^+X. Without going into details, we will simply note that the average Ne-2s orbital energy in NeH^+Ne is about −2.286 a.u. while the corresponding orbital energies in Ne and Ne^+H are −1.706 and −2.443 a.u., respectively. The fractional change for the intermediate is about 0.21 and can be compared with f^0 (0.2761) calculated from the proton affinity and the intrinsic barrier in Table IV. This feature is general for all the reactions discussed here, and it was also found that these orbital f's change with ΔE in the same qualitative fashion as indicated in Figure 2. A complete treatment of this phenomenon will be reported later. Preliminary results indicate that a similar effect is operating in the much more complicated system ($HC{\equiv}C{-}CH_2^- + H{-}CH_2{-}C{\equiv}N$).

[67] The total bond orders for $HeHNe^+$, $HeHAr^+$, and $NeHAr^+$ are 0.1136 + 0.8478 = 0.9614; 0.0393 + 0.9674 = 1.0067; and 0.5132 + 0.4775 = 0.9907, respectively. Bond orders are calculated from Pauling's relationship, $n_{XH} = \exp(-a_{XH}\Delta r_{XH})$ where a_{XH} (X = He, Ne, Ar) is obtained from the identity complex by arbitrarily setting $n = {}^1/_2$. Changes in individual bond order (δn_{XH}, δn_{YH}) compensate to a high degree, resulting in approximately constant total bond order ($\delta n_{XH} + \delta n_{YH} \simeq 0$).

Table VI. Barriers of Cross Reactions–Proton and and Methyl Transfer

	$X{-}CH_3{-}Y^-$			$X{-}H{-}Y^-$
ΔE, kcal	-58.88^b	-52.85^c	-53.79^d	23.36^e
$\Delta E^{\ddagger}_0$	41.18	33.90	32.64	−21.605
$\Delta E^{\ddagger}$	15.64	11.99	9.98	−10.39
$\Delta E^{\ddagger}{}_{\text{Marcus}}$	17.00	12.62	11.26	−11.50
$\Delta E^{\ddagger}{}_{\sin}{}^a$	13.35	9.30	7.87	−10.21
$\Delta E^{\ddagger}{}_{\arctan}{}^a$	15.67	11.59	10.32	−10.82
$\Delta E^{\ddagger}{}_{\tanh}{}^a$	14.30	10.28	8.96	−10.43

[a] $\epsilon = 1$. [b] $F{-}CH_3{-}H^-$ (Dedieu and Veillard, ref 67). The calculated potential surfaces for these reactions show stable intermediates between the transition state and the separated reactants. The estimates of ΔE, $\Delta E^{\ddagger}_0$, $\Delta E^{\ddagger}$ are based on the intermediates using data from Table VI and Figures 3–6 (ref 68). [c] F. Keil and R. Ahlrichs (ref 70). SCF result using a large Gaussian basis set. [d] Same as *c*, except an estimate of the correlation energy is included based on the CEPA technique. The agreement between Keil and Ahlrichs' SCF barriers and the barriers calculated from Marcus' equation and eq 24–27 is partly fortuitous since no correction has been made for any intermediates between the transition state and the isolated reactants. [e] $[H{-}C{\equiv}C{-}CH_2{-}H{-}CH_2{-}C{\equiv}N]^-$. These calculations are preliminary and were carried out at the 3-G level. The geometries of the identity transition states have been carefully optimized with respect to the X–H and H–Y distances and partially optimized with respect to C–C and C–N bond lengths and the bond angles around the α carbons. The structure of the transition state for the cross reaction was initially taken to be hemistructural, and then the X–H and H–Y distances were re-optimized. The resulting energy change was negligible. A more refined treatment will be presented.

geometry, and its energy is about 0.1 kcal below the mean energy of ArH^+Ar and NeH^+Ne. This agreement is particularly interesting since ΔE for the cross reaction is over 18 kcal and suggests that the hemistructural relationship[38] will hold over an appreciable range of structure.

Before closing, it is worthwhile pointing out an interesting result obtained by Dedieu and Veillard[68] for the displacement of fluoride by hydride from methylfluoride. They calculated the barrier of this reaction by using a large Gaussian basis set with limited geometry optimization and CI.

$$H^- + CH_3F \rightleftharpoons H{-}CH_3 + F^- \qquad (31)$$

The hydride identity barrier is 62.75 kcal, the fluoride identity barrier is 19.6 kcal, and ΔE is −58.9 kcal. The barrier for the unsymmetrical cross reaction (eq 31) is 15.6 kcal and Marcus' equation predicts a barrier too high by 1.4 kcal, while the arctan equation agrees within 0.03 kcal (Table VI). Also included are results from two other SCF calculations for the same reaction and preliminary results for the proton-transfer reaction between $H{-}C{\equiv}C{-}CH_2^- + H{-}CH_2{-}C{\equiv}N$. Agreement is reasonable in all cases: 0.63–1.28 kcal for Marcus' equation and 0.34–0.43 kcal for the arctan equation.

It should be noted that, in a pioneering study, Pellerite and Brauman[69] have recently applied Marcus' equation to gas-phase nucleophilic displacements and have correlated leaving group ability with the height of the intrinsic barrier. This work represents the first application of Marcus' equation to an experimental, gas-phase, S_N-2 reaction and has, in addition to other important contributions, called attention to the importance of both kinetic and thermodynamic contributions to the barriers of S_N-2 reactions. Notable work by Lewis[71] and by Kreevoy and Albery[72] on solution phase S_N-2 reactions has also emphasized the role of kinetic and thermodynamic contributions. Equation 23 has also been shown to describe experimental gas-phase well depths of 51 proton-bound dimers of anions, amines, and neutral hydrides.[41] Marcus' equation has also been used to correlate computed (4-31G) barriers to S_N-2 reactions.[41,73]

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