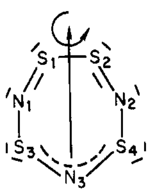

This is the only structure that can be built from the structural elements listed above which preserves the diagrammed rotational axis. It predicts the molecule ion to be a 6π system. The Banister counting method predicts the ion to contain 10π electrons. The presence of 10π electrons is difficult to accept since the molecule clearly contains no S–S multiple bonds (d_{S-S} observed = 2.06 Å) and thus the 10π electrons must be equally distributed over the six possible N–S segments of the ring. Our predicted structure resolves this problem. The structure predicted above implies that the electronic environment of N_3 is different from that of N_1 or N_2 which in turn are equivalent to each other. The four sulfur atoms are pairwise equivalent (S_1 is the same as S_2; S_3 is the same as S_4). These equivalencies should be reflected in the photoelectronic spectrum of the molecule ion and also in the chemistry. The molecule also possesses a four-electron-three-center π-type charge distribution ($S_3N_3S_4$) and two isolated S–N normal π bonds.

Supplementary Material Available: CNDO/2 results (population analysis) and atomic orbital coefficient for localized molecular orbitals for all four-, five-, and six-membered ring compounds discussed herein (26 pages). Ordering information is given on any current masthead page.

Kinetic and Thermodynamic Contributions to Energy Barriers and Energy Wells: Application to Proton-Bound Dimers in Gas-Phase Proton-Transfer Reactions

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Abstract: A previously reported equation for predicting energy barriers yields Marcus' equation for electron transfer as a special case and is shown to be suitable for estimating the stabilities of proton-bound dimers of neutral molecules and anions in the gas phase. The average deviation between calculated and experimental well depths of 51 proton-bound dimers is about 0.6 kcal. In many cases, the energy of the proton-bound dimer (A–H–C) is simply the average of the energies of the two symmetrical dimers (A–H–A and C–H–C). In other cases a nonlinear correction becomes important. It is significant that either barrier heights or well depths for group-transfer reactions can be expressed in terms of the thermodynamics of the overall reaction (A–B + C → A + B–C) and the barrier heights (or well depths) of two thermoneutral identity reactions (A–B + A → A + B–A and C–B + C → C + B–C).

I. Energy Barriers and Energy Wells. Some Common Elements

A. General Equation for Describing Energy Barriers. Recently it has been found that energy barriers for group-transfer reactions are closely related to the overall thermodynamics and to the barriers of two related identity reactions.[1] For example, the barrier for a reaction A–B + C → A + B–C can be expressed as:

$$\Delta E^{\ddagger} = \Delta E_0^{\ddagger}(1 - g_2(\tau)) + {}^1\!/_2\Delta E(1 + g_1(\tau)) \qquad (1)$$

where $\Delta E_0^{\ddagger}$ (called the intrinsic barrier) is the average of the barriers for the identity reactions A–B + A → A + B–A and C–B + C → C + B–C, ΔE is the difference in energy between products and reactants, and g_2 and g_1 are even and odd functions[2] of τ, which in turn is a function of $\Delta E_0^{\ddagger}$ and ΔE. Possible choices for τ include:

$$\tau = \Delta E/4\Delta E_0^{\ddagger} \qquad |\Delta E/\Delta E_0^{\ddagger}| \leq 4 \qquad (2)$$

$$\tau = \sin(\Delta E/2\Delta E_0^{\ddagger}) \qquad |\Delta E/\Delta E_0^{\ddagger}| \leq \pi \qquad (3)$$

$$\tau = (2/\pi)\arctan(\pi\Delta E/4\Delta E_0^{\ddagger}) \qquad (4)$$

$$\tau = \tanh(\Delta E/2\Delta E_0^{\ddagger}) \qquad (5)$$

These relationships are shown graphically in Figure 1.

B. Marcus' Equation for Electron Transfer Is a Special Case. The simplest odd and even functions of τ are the monomials τ and τ^2, which on substitution in eq 1 give

$$\Delta E^{\ddagger} = \Delta E_0^{\ddagger}(1 - \tau^2) + {}^1\!/_2\Delta E(1 + \tau) \qquad (6)$$

Equation 6 is limited to the range $|\Delta E| \leq 4|\Delta E^{\ddagger}_0|$ which interestingly enough is also a feature of Marcus' equation.[3] In fact, substitution of eq 2 into eq 6 leads to Marcus' equation:[4]

$$\Delta E^{\ddagger}_{\text{Marcus}} = \Delta E_0^{\ddagger} + {}^1\!/_2\Delta E + (\Delta E)^2/16\Delta E_0^{\ddagger} \qquad (7)$$

C. τ Is a "Nonadditivity" Parameter. It should be noted that when $\tau = 0$, the energy of A–B–C is simply the average of the energies of A–B–A and C–B–C.[1] Under such conditions the barrier for the reaction A–B + C → A + B–C is given by:

$$\Delta E^{\ddagger}_{\text{additive}} = \Delta E_0^{\ddagger} + {}^1\!/_2\Delta E \qquad (8)$$

The ${}^1/_2\Delta E$ term can be regarded as the thermodynamic contribution to the barrier, since it is directly related to the thermodynamics of the overall reaction. The other term, $\Delta E_0^{\ddagger}$, can be

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(1) J. R. Murdoch and D. E. Magnoli, *J. Am. Chem. Soc.*, in press. This material was also presented at the 5th IUPAC Conference on Physical Organic Chemistry, Santa Cruz, Calif., Aug 1980.

(2) An odd function of τ is one which can be expressed in terms of odd powers of τ, and an even function is one which can be expressed in terms of even powers of τ. For $\tau \to 1$, g_1 and g_2 approach unity, and for $\tau \to -1$, $-g_1$ and g_2 approach unity. When $\tau = 0$, g_1 and g_2 equal zero. See ref 1 for details.

(3) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).

(4) The fact that ΔE is confined to a finite range has troubled certain authors, and this problem has been discussed elsewhere.[1] It can be shown[1] that the choice of $g_1(\tau)$ and $g_2(\tau)$ determines whether ΔE is confined to a finite or to an infinite range. Two choices for $g_1(\tau)$ and $g_2(\tau)$ which lead to an infinite range for ΔE are: $g_1(\tau) = {}^3/_2\tau - {}^1/_2\tau^3$; $g_2(\tau) = \tau^2$ and $g_1(\tau) = \sin \pi\tau/2$; $g_2(\tau) = 1 - \cos \pi\tau/2$.

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Table I.[a] Observed and Calculated Values of $\Delta H^{\ddagger}$ for Some Proton-Transfer Reactions

	$\Delta H^{\ddagger}{}_{\text{iden}}{}^{b,d}$	$\Delta H_0^{\ddagger}{}^{c,e}$	$\Delta H^{\circ}{}^{b,f}$	$\Delta H^{\ddagger}{}_{\text{add}}{}^{c,g}$	$\Delta H^{\ddagger}{}_{\text{arctan}}{}^{c,h}$	$\Delta H^{\ddagger}{}_{\text{Marcus}}{}^{c,i}$	$\Delta H^{\ddagger}{}_{\text{obsd}}{}^{b,j}$	$\Delta H^{\ddagger}{}^{c,k}$
pyrrolidine/Me$_3$N	-21.5/-19.3	-20.4	0.0	-20.4	-20.4	-20.4	-20.1	0.3
sec-BuNH$_2$/Me$_2$NH	-20.3/-20.8	-20.55	0.0	-20.55	-20.55	-20.55	-20.8	-0.25
i-PrNH$_2$/*i*-BuNH$_2$	-20.6/-20.2	-20.4	-0.1	-20.45	-20.45	-20.45	-20.5	-0.05
pyridine/*sec*-BuNH$_2$	-21.6/-20.3	-20.95	-0.1	-21.0	-21.0	-21.0	-20.9	0.1
pyridine/Me$_2$NH	-21.6/-20.8	-21.2	-0.1	-21.25	-21.25	-21.25	-23.3	-2.05
allyl-NH$_2$/EtNH$_2$	-20.9/-20.9	-20.9	-0.6	-21.2	-21.2	-21.2	-21.3	-0.1
Et$_2$NH/piperidine	-19.6/-20.7	-20.15	-0.3	-20.3	-20.3	-20.3	-20.4	-0.1
n-BuNH$_2$/*i*-PrNH$_2$	-21.1/-20.2	-20.65	-0.4	-20.85	-20.85	-20.85	-20.8	+0.05
n-PrNH$_2$/*n*-BuNH$_2$	-21.1/-20.8	-20.95	-0.5	-21.2	-21.2	-21.2	-20.6	0.6
sec-BuNH$_2$/c-hexyl-NH$_2$	-20.3/-21.2	-20.75	-0.8	-21.15	-21.15	-21.15	-21.1	0.05
Me$_3$N/Et$_2$NH	-19.3/-19.6	-19.45	-0.8	-19.85	-19.85	-19.85	-19.7	0.15
pyridine/c-hexyl-NH$_2$	-21.6/-21.2	-21.4	-0.9	-21.85	-21.85	-21.85	-21.8	0.05
i-BuNH$_2$/pyridine	-20.6/-21.6	-21.1	-0.9	-21.55	-21.55	-21.55	-21.3	0.25
i-BuNH$_2$/Me$_2$NH	-20.6/-20.8	-20.7	-1.0	-21.2	-21.2	-21.2	-21.6	-0.4
n-PrNH$_2$/*i*-BuNH$_2$	-20.8/-20.6	-20.7	-1.0	-21.2	-21.2	-21.2	-21.3	-0.1
pyrrolidine/piperidine	-21.5/-20.7	-21.1	-1.1	-21.65	-21.65	-21.65	-21.6	0.05
i-PrNH$_2$/Me$_2$NH	-20.2/-20.8	-20.5	-1.1	-21.05	-21.05	-21.05	-21.5	-0.45
i-PrNH$_2$/*sec*-BuNH$_2$	-20.2/-20.3	-20.25	-1.1	-20.8	-20.8	-20.8	-20.8	0.0
Me$_3$N/piperidine	-19.3/-20.7	-20.00	-1.1	-20.55	-20.55	-20.55	-20.3	0.25
piperdine/Me$_2$NEt	-20.7/-19.0	-19.85	-1.2	-20.45	-20.45	-20.45	-20.7	-0.25
Et-NH$_2$/*n*-PrNH$_2$	-20.9/-20.8	-20.85	-1.4	-21.55	-21.55	-21.55	-21.5	0.05
n-BuNH$_2$/Me$_2$NH	-21.1/-20.8	-20.95	-1.5	-21.7	-21.7	-21.7	-22.2	-0.5
MeEtNH/pyrrolidine	-20.5/-21.5	-21.0	-1.7	-21.85	-21.85	-21.85	-21.6	0.25
i-PrNH$_2$/c-hexyl-NH$_2$	-20.2/-21.2	-20.7	-1.9	-21.65	-21.65	-21.65	-21.7	-0.05
c-hexyl-NH$_2$/Et$_2$NH	-21.2/-19.6	-20.4	-3.8	-22.3	-22.3	-22.3	-23.5	-1.2
n-PrNH$_2$/Me$_2$NH	-20.8/-20.8	-20.8	-2.0	-21.8	-21.8	-21.8	-22.3	-0.5
pyridine/MeEtNH	-21.6/-20.5	-21.05	-2.2	-22.15	-22.15	-22.15	-23.1	-0.95
Me$_2$NH/azetidine	-20.8/-21.9	-21.35	-2.2	-22.45	-22.45	-22.45	-22.4	0.05
pyridine/azetidine	-21.6/-21.9	-21.75	-2.3	-22.9	-22.9	-22.9	-23.5	-0.6
EtNH$_2$/*i*-PrNH$_2$	-20.9/-20.2	-20.55	-2.3	-21.7	-21.7	-21.7	-21.9	-0.2
MeNH$_2$/allyl-NH$_2$	-21.6/-20.9	-21.25	-2.4	-22.45	-22.45	-22.45	-22.5	-0.05
azetidine/Et$_2$NH	-21.9/-19.6	-20.75	-2.4	-21.95	-21.95	-21.95	-22.3	-0.35
MeEtNH/Et$_2$NH	-20.5/-19.6	-20.05	-2.5	-21.3	-21.3	-21.3	-21.4	-0.1
Me$_2$NH/MeEtNH	-20.8/-20.5	-20.65	-2.1	-21.70	-21.70	-21.70	-21.8	-0.1
H$_2$O/H$_2$S	-31.6^l/-15.4^l	-23.5	-3.0^l	-25.0	-25.0	-25.0	-24.9^l	0.1
MeNH$_2$/EtNH$_2$	-21.6/-20.9	-21.25	-3.0	-22.75	-22.75	-22.75	-22.8	-0.05
c-hexyl-NH$_2$/Me$_3$N	-21.2/-19.3	-20.25	-3.0	-21.75	-21.75	-21.8	-22.8	-1.0
Me$_2$NH/Me$_3$N	-20.8/-19.3	-20.05	-3.8	-21.95	-21.95	-22.0	-22.3	-0.3
piperdine/*N*-Me-piperidine	-20.7/-18.2	-19.45	-3.4	-21.15	-21.15	-21.2	-21.9	-0.7
pyridine/Me$_3$N	-21.6/-19.3	-20.45	-3.9	-22.4	-22.4	-22.45	-24.4	-1.95
azetidine/Me$_2$NEt	-21.9/-19.0	-20.45	-3.9	-22.4	-22.4	-22.45	-23.2	-0.75
piperidine/*i*-Pr$_2$NH	-20.7/-15.4	-18.05	-3.5	-19.8	-19.8	-19.85	-20.6	-0.75
Et$_2$NH/*i*-Pr$_2$NH	-19.6/-15.4	-17.5	-3.8	-19.4	-19.4	-19.45	-20.1	-0.65
pyrrolidine/*N*-Me-piperidine	-21.5/-18.2	-19.85	-4.5	-22.1	-22.1	-22.15	-23.1	-0.95

pyridine/Et_2NH	−21.6/−19.6	−20.6	−4.7	−22.95	−22.95	−23.0	−24.9	−1.9
pyrrolidine/*i*-Pr_2NH	−21.5/−15.4	−18.45	−4.6	−20.75	−20.75	−20.8	−22.0	−1.2
azetidine/*i*-Pr_2NH	−21.9/−15.4	−18.65	−6.2	−21.75	−21.75	−21.9	−24.3	−2.4
Br^-/Cl^-	$-23.7^m/-18^n$	−20.85	-9.7^n	−25.7	−25.75	−26.0	-25.7^n	0.3
F^-/OH^-	$-37^p/-24^n$	−30.5	-21.0^n	−41.0	−41.3	−41.9	-44^n	−2.1
H_2O/NH_3	$-31.6^l/-25^o$	−28.3	-32^o	−44.3	−45.65	−46.55	-49.2^o	−2.65
Cl^-/F^-	$-23.7^n/-37^p$	−30.35	-36^n	−48.35	−50.15	−51.0	-50^n	1.0

[a] The reaction under consideration is the transfer of a proton from the first base of a pair to the second. All values in kcal/mol. [b] All experimental values are from ref 8 unless otherwise noted. [c] Calculated values reported to nearest 0.05 kcal/mol. [d] $\Delta H^{\ddagger}{}_{\text{iden}}$ is the barrier for the identity reaction $AH^+ + A \rightarrow A + HA^+$. [e] $\Delta H^{\ddagger}_0$ is the average of the two identity barriers. [f] $\Delta H°$ is the difference in energy of the products and the reactants. [g] From eq 8. [h] From eq 4 and 6. [i] From eq 7. [j] Experimental value of $\Delta H^{\ddagger}$. [k] $\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}{}_{\text{obsd}} - \Delta H^{\ddagger}{}_{\text{Marcus}}$. [l] From ref 9. [m] From ref 11. [n] From ref 10. [o] From ref 13. [p] From ref 12.

Table II.[a] Observed and Calculated Values of $\Delta H^{\ddagger}$ for Proton Transfer to OH^- from Cl^- and Br^-

	$\Delta H^{\ddagger}{}_{\text{iden}}{}^{d,q}$	$\Delta H_0{}^{c,e}$	$\Delta H°{}^{f,q}$	$\Delta H^{\ddagger}{}_{\text{add}}{}^{c,g}$	$\Delta H^{\ddagger}{}_{\text{arctan}}{}^{c,h}$	$\Delta H^{\ddagger}{}_{\text{Marcus}}{}^{c,i}$	$\Delta H^{\ddagger}{}_{\text{obsd}}{}^{j,q}$	$\Delta\Delta H^{\ddagger}{}^{c,k}$
Cl^- OH^-	-23.7^m −24	−23.85	−57	−52.35	−60.65	−60.85	−70.1	−9.25
Br^- OH^-	−18 −24	−21	−66.7	−54.4	−67.55	−67.7	−79.3	−11.6

[a] See corresponding footnotes in Table I. [b] All experimental values are from ref 10 unless otherwise noted.

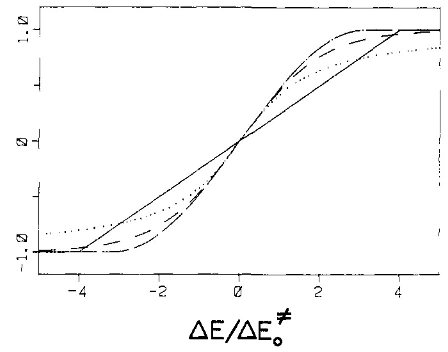

Figure 1. Possible behavior of τ as a function of $\Delta E/\Delta E^{\ddagger}_0$: (—) Marcus (eq 2), (– –) sin (eq 3), (- - -) arctan (eq 4), (. . .) tanh (eq 5). τ has been chosen to have limiting values of −1 and 1, and limiting slopes of 0. For simple sigmoid functions (i.e., those with only one inflection point), the slope at $\Delta E/\Delta E^{\ddagger}_0 = 0$ is constrained to be between the Marcus slope (which is 1/4) and the slope of the other lines (which is 1/2). For further discussion, see ref 1.

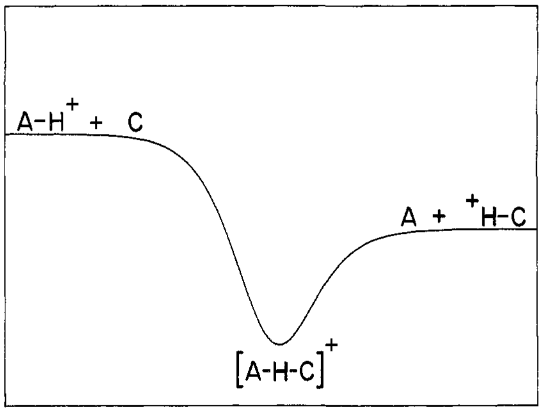

Figure 2. Energetic relationships for a proton-bound dimer in a single minimum potential well.

considered the *kinetic* contribution, since it is dependent on the *barrier heights* (or well depths) of two thermoneutral identity reactions.

Other work[1,5,6] shows that energy additivity, as well as some nonadditivity, is a consequence of a hemistructural relationship.[7] As the hemistructural relationship breaks down, nonadditive energy terms become increasingly important, and it was found that nonzero values of τ in eq 1 or 6 could empirically account for the nonadditivity.[1]

D. Are Energy Wells Equivalent to "Inverted" Energy Barriers? The derivation of eq 1 assumes a stationary point on the A–B–C potential surface between the reactants (A–B + C) and the products (A + B–C), but makes no distinction between a transition state or a stable intermediate. Special cases of eq 1 (e.g., eq 7) have long been applied to predicting barriers for group and electron-transfer reactions (see references in ref 1), and in another paper, application of eq 1 and 7 has been made to barriers and well depths calculated by SCF methods.[1] In the present contribution, we wish to report an application of eq 1 and 7 to experimental, gas-phase proton-transfer reactions which involve stable intermediates.

II. Application of Eq 1 to Proton-Bound Dimers

A. Experiment vs. Theory. An Energy Well Example. It is known[8-13] that neutral molecules and anions form proton-bound

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(5) J. R. Murdoch, *J. Am. Chem. Soc.*, in press.

(6) J. R. Murdoch and D. E. Magnoli, *J. Am. Chem. Soc.*, in press.

(7) A molecule ABC is defined to be hemistructural to two parent structures ABA and CBC if the nuclei of the AB fragments of ABC and ABA are directly superimposable, and if the nuclei of the BC fragments of ABC and of CBC are superimposable. For a more general definition, see ref 5.

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

(9) K. Hiraoka and P. Kebarle, *Can. J. Chem.*, **55**, 24 (1977).

dimers in the gas phase:

$$H_3O^+ + NH_3 \rightleftarrows H_2O\text{-}H^+\text{-}NH_3 \rightleftarrows H_2O + NH_4^+$$

In this type of reaction, the proton-bound dimer is more stable than either set of products, and, consequently, it lies at an energy minimum. Derivation of eq 1 allows application to energy minima as well as to barriers (see Figure 2).[1] The results (in terms of $\Delta H°$, rather than ΔE) for various gas-phase proton-transfer-reactions are summarized in Table I, where the reactions are listed in order of increasing $\Delta H°/\Delta H^{\ddagger}_0$. Since most of the equilibria have very small $\Delta H°/\Delta H^{\ddagger}_0$ ($\sim$0.2), calculated values of $\Delta H^{\ddagger}$ are nearly independent of the expressions used for τ, g_1, and g_2, so that only the $\Delta H^{\ddagger}{}_{\text{Marcus}}$ and the $\Delta H^{\ddagger}{}_{\text{arctan}}$ from eq 6 are given. A detailed comparison of results obtained from various choices of τ, g_1, and g_2 will be given elsewhere.

The table shows that eq 6 is in good agreement with $\Delta H^{\ddagger}{}_{\text{obsd}}$, with an average deviation of 0.58 kcal/mol for the 51 reactions. A least-squares analysis of $\Delta H^{\ddagger}{}_{\text{Marcus}}$ and $\Delta H^{\ddagger}{}_{\text{obsd}}$ gives a linear correlation (correlation coefficient = 0.993, slope = 0.960 ± 0.02, intercept = 0.5 ± 0.5) with a standard deviation of 0.9 kcal/mol. The results indicate that eq 7 underestimates the stability of the proton-bound dimer and that this discrepancy increases somewhat with increasing $\Delta H°/\Delta H^{\ddagger}_0$. This trend may be real or may reflect small systematic errors in the experimental measurements, which are most accurate for $\Delta H° \sim 0$.[8] Two reactions which do not fit eq 6 are shown in Table II. The large discrepancy between $\Delta H^{\ddagger}{}_{\text{Marcus}}$ and $\Delta H^{\ddagger}{}_{\text{obsd}}$ could have experimental or theoretical origins.[5] One possibility includes a double well potential surface.[14]

B. Additivity Is a Good Limiting Description. For those reactions where $\Delta H°/\Delta H^{\ddagger}{}_0$ is close to zero, the additive approximation (eq 8) gives a reasonably good description of the well depths. This is a significant observation since the variations in the amines involve substantial changes in the size of the alkyl groups. Particularly noticeable is the absence of any breakdown into "families" according to type of amine (e.g., primary, secondary, tertiary, aliphatic, aromatic, etc.). This additivity also has an important implication for the observation[8] that $\Delta G°$ for the reaction

$$A\text{-}H\text{-}A^+ \rightleftarrows 2A + H^+ \qquad \Delta G° \text{ (dimer)}$$

generally follows $\Delta G°$ for the reaction:

$$A\text{-}H^+ \rightleftarrows A + H^+ \qquad \Delta G° \text{ (monomer)}$$

where A is an amine. A comparison of data for diisopropylamine and piperidine shows that diisopropylamine is *more* basic than piperidine by 3.5 kcal/mol when basicity is defined in terms of $\Delta G°$ (monomer). If $\Delta G°$ (dimer) is used as the basicity standard, diisopropylamine is *less* basic than piperidine by 2 kcal/mol.[8] Aue and Bowers interpret this discrepancy (5.5 kcal) in terms of steric interactions between the two amine groups in the dimer which are absent in the monomer.[8] The results in Table I and eq 8[1,6] show that the dissociation energy[15] for AHC (piperidine–H$^+$–diisopropylamine) is close to the average of the dissociation energies[15] of AHA and CHC (within 0.75 kcal/mol). Consequently, it would appear that any steric effect is either additive, constant, or negligible for AHA, AHC, and CHC.[16,17]

C. Nonadditivity May Also Be Important. For those cases in Table I where τ is fairly large, the correction due to the nonadditive part of eq 1 alters $\Delta H^{\ddagger}{}_{\text{add}}$ in the right direction. An example is the H_2O/NH_3 reaction: $\Delta H^{\ddagger}{}_{\text{add}} = -44.3$ kcal/mol; $\Delta H^{\ddagger}{}_{\text{Marcus}} = -46.6$ kcal/mol; $\Delta H^{\ddagger}{}_{\text{obsd}} = -49.2$ kcal/mol. A similar result is found for the Cl^-/F^- reaction: $\Delta H^{\ddagger}{}_{\text{add}} = -48.35$ kcal/mol, $\Delta H^{\ddagger}{}_{\text{Marcus}} = -51.0$ kcal/mol; $\Delta H^{\ddagger}{}_{\text{obsd}} = -50$ kcal/mol. In each case, the nonadditive correction serves to increase the calculated well depth of the proton-bound dimer. The effect has also been noted in several SCF calculations of proton bound anions[1] and rare gas atoms.[1] The SCF calculations (4–31G) of Allen for proton-bound hydrides[18] show similar trends.

D. Deviations May Occur for Double Minima Potential Wells. Allen's examples generally exhibit double minima and consequently will not be discussed in detail. However, it may be significant that the SCF (4–31G) well depths for the unsymmetrical proton-bound dimers (i.e., the deepest well) are about 5 to 15 kcal lower than predicted by Marcus' equation and closely follow the pattern seen in Table II. This includes the example of $H_2O\text{-}H\text{-}NH_3^+$ for which calculation gives a double minima potential well, and $\Delta E^{\ddagger}$ shows a substantial negative deviation from Marcus' equation (7.6 kcal). The experimental value is in closer agreement (−2.65 kcal, Table I), but whether these discrepancies have anything to do with multiple minima is simple speculation for the moment.[19] The following example (a *barrier* application) as well as previous SCF calculations for proton-bound dimers of rare gas atoms[1] show that large values of $\Delta E/\Delta E^{\ddagger}_0$ are not sufficient to produce substantial discrepancies from Marcus' equation.

III. Application of Eq 1 to an S_N2 Displacement. A Barrier Problem

The displacement of fluoride from fluoromethane by hydride is an example where nonadditivity is important.

$$H^- + CH_3\text{-}F \rightleftarrows H\text{-}CH_3 + F^-$$

Dedieu and Veillard[20] calculated the barrier of the reaction using a large Gaussian basis set with partial geometry optimization. ΔE for the reaction is −58.88 kcal/mol,[1] and the barrier is 15.64 kcal/mol. The hydride identity reaction has a barrier of 62.8 kcal/mol, and the barrier for the fluoride identity reaction is 19.6 kcal/mol. The barrier calculated from the additive terms of eq 1 is 11.73 kcal/mol, and the correction for nonadditivity is 5.27 kcal/mol (Marcus' equation). The sum yields a predicted barrier of 17 kcal/mol, which is in reasonable agreement with the cal-

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(10) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **93**, 7139 (1971).

(11) R. Yamdagni and P. Kebarle, *Can. J. Chem.*, **52**, 2449 (1974).

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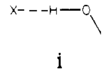
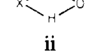
(14) The use of eq 2–5 in conjunction with eq 1 assumes a single energy maximum or minimum between the isolated reactants and products. In principle, eq 1–5 could be applied to a double minimum potential well by a suitable redefinition of ΔE and $\Delta E^{\ddagger}$, provided that the "identity" structures (e.g., $Br\text{-}H\text{-}Br^-$ and $HO\text{-}H\text{-}OH^-$) and the "cross" structure (e.g., $Br\text{-}H\text{-}OH^-$) all exhibit double minima. If the two symmetrical structures (e.g., $Br\text{-}H\text{-}Br^-$ and $HO\text{-}H\text{-}OH^-$) have a single energy minimum and the unsymmetrical structure ($Br\text{-}H\text{-}OH^-$) shows double minima, the approximate error in $\Delta H^{\ddagger}{}_{\text{calcd}}$ would be given by the difference between the lower minimum and the maximum separating the minima. The finding (H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **58**, 5627 (1973)) that structures such as i are favored for small anions (F^-) whereas structures such as ii are preferred for large anions (Cl^-) may also be pertinent to the deviations seen in Table II. An alternative (and wild) speculation might be that the unsymmetrical structure may have another minimum (e.g., $H\text{-}Br\text{-}OH^-$) lower in energy than the hemistructural geometry (viz., $Br\text{-}H\text{-}OH^-$). The main point is that nonhemistructural maxima or minima may indicate significant contributions from second or higher order corrections to the MO coefficients,[5] which are not taken into account in the derivation of eq 1.[1]


i


ii

(15) Dissociation refers to the process AHB → A + H^+ + B.

(16) It should be emphasized that additivity does not imply the absence of A/C interactions. This apparent paradox is widespread (ref 5), and a theoretical treatment has been presented (ref 5 and 6).

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(18) D. J. Desmeules and L. C. Allen, *J. Chem. Phys.*, **72**, 4731 (1980).

(19) Following ref 1, the hemistructural relationship can be applied to a double minimum potential well, and it can be shown that the deeper well will be lower than the prediction of eq 8 by $^1/_2\Delta E_w$, where ΔE_w represents the energy difference between A–HC and AH–C which occur as the two stable intermediates in the overall reaction, AH + C ⇌ AH–C ⇌ A–HC ⇌ A + HC. As the hemistructural relationship breaks down, the deviations from predictions based on eq 7 and the single well assumption may increase or decrease depending on the relationship between ΔE and ΔE_w. The effect of a double minimum on the relationship between ΔE and the well depths of the symmetrical exchange reactions (e.g., AH + A ⇌ AH–A ⇌ A–HA ⇌ A + HA) is under investigation.

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

culated SCF result (15.64 kcal/mol). The nonadditivity correction based on the arctan equation is 3.94 kcal which gives a barrier (15.67 kcal/mol) in somewhat better agreement with Dedieu and Veillard's SCF result (15.64 kcal/mol).

IV. Conclusions

Equation 1 is based on the behavior[5] of ΔE and neglects zero-point energies as well as enthalpy corrections from 0 K. We have found, using data of Aue and Bowers,[8] that eq 1 and 6 work fairly well for $\Delta H°$, and somewhat less well for $\Delta G°$. This is not unreasonable[21] since the progression from $\Delta E \rightarrow \Delta H° \rightarrow \Delta G°$ involves introducing more thermodynamic information at each step. The degree of applicability of eq 1 to $\Delta H°$ or $\Delta G°$ will require further examination. Nonetheless, we find it significant that the same equation (i.e., eq 1) which has been shown[1] to account for *barriers* to group transfer reactions can also account for *well depths* of stable hydrogen-bonded intermediates. The role of multiple minima or maxima in altering the prediction of eq 1 remains an important question,[19] and a more refined theoretical treatment is in progress.

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Ab Initio Studies of (1,2)-Hydrogen Migrations in Open-Shell Hydrocarbons: Vinyl Radical, Ethyl Radical, and Triplet Methylcarbene†

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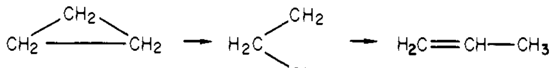
Abstract: Ab initio, POL–CI calculations on the barriers to hydrogen migration in the title compounds are reported. For C_2H_3, C_2H_5, and CH_3CH the predicted barriers are 57, 46, and 53 kcal/mol, respectively. For the first two molecules barriers to C–H bond cleavage are also calculated and found to be lower than the migration barriers. A qualitative analysis of the wave functions indicates that the high migration barriers are due to a geometrical constraint placed on the electronic structure of the transition state. A comparison to hydrogen migration in a closed-shell molecule (vinylidene–acetylene) is also presented.

I. Introduction

It has long been recognized that (1,2)-hydrogen migrations are, at least in principle, viable pathways for rearrangement of alkyl radicals.[1] Many attempts have been made to measure rate constants, activation energies and *A* factors for these rearrangements in order to determine if these reactions play an important role in the chemistry of free radicals.[2–4] To our knowledge however none of these attempts have led to unambiguous results. The primary difficulty here is the extreme complexity of the chemical systems involved. The high reactivity of free radicals leads to a large number of possible reaction pathways, all of which must be considered in any meaningful analysis of the data.[5]

In hydrocarbon combustion chemistry, the importance of (1,4)- and (1,5)-hydrogen migrations in alkyl radicals is well recognized. However, the question of whether or not (1,2) and (1,3) migrations contribute significantly to the flame chemistry of alkyl radicals has not yet been satisfactorily answered. It has generally been assumed though that the rates of these arrangements are too slow to compete with bimolecular reactions under typical flame conditions.[5–7]

A closely related question is whether or not (1,2) migrations occur in biradicals. Here the question is complicated by the existence of two nearly degenerate states, a singlet and a triplet. There is considerable evidence supporting the occurrence of (1,2) migrations in singlet biradicals, particularly in those rearrangements which are extremely exothermic.[8] For example the thermal decomposition of cyclopropane[9] has been shown to require an activation energy only slightly larger than that necessary to break the C–C bond. Assuming the mechanism involves a biradical,



(1)

This would imply that the barrier to (1,2) migration in the biradical is near zero.

For triplet biradicals the evidence for (1,2)-hydrogen migrations is less convincing. This may be due in part to the difficulty of generating triplet biradicals and to the rapidity with which these species cross to singlet surfaces. There are however several combustion reactions which presumably involve triplet biradicals for which (1,2)-hydrogen migrations have been postulated. One

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