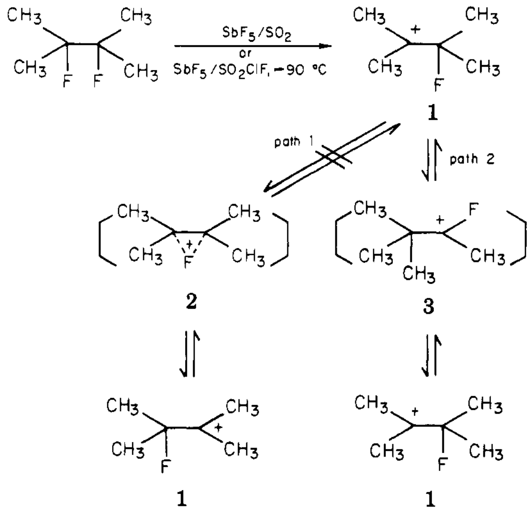
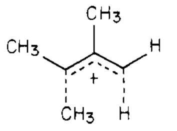
Scheme I



such a structure has been proposed by Clark, based on theoretical calculations.[7] If the exchange involves only rapid 1,2-methyl migration, then the 3,3-dimethyl-2-fluoro-2-butyl cation ((1-fluoro-1-*tert*-butyl)ethyl cation) **3** should be involved. These two possibilities, however, could not be distinguished on the basis of ^{1}H and ^{19}F NMR studies.[6]

We now report a ^{13}C NMR spectroscopic study of ion **1** in SbF_5/SO_2ClF solution that clearly rules out equilibration through rapid intramolecular fluorine exchange. The proton-decoupled 20-MHz ^{13}C NMR spectrum of ion **1** at −80 °C shows absorptions at δ 324.3 (C^+, broad <20 Hz), 115.2 (β CF, doublet, $J = 208.8$ Hz) and 36.3 (av CH_3, doublet, $J = 13.2$ Hz). The observation of three signals as opposed to two clearly supports the methyl migration pathway (path 2) through 1-fluoro-1-*tert*-butylethyl cation **3**. Further support comes from the observation of a highly deshielded carbocationic center, as well as a strongly coupled β-fluoro carbon. Attempts to freeze out the rapid methyl migration, even at −120 °C, were unsuccessful. There is no appreciable change in the NMR spectrum between −60 and −120 °C, except for some viscosity-induced line broadening, indicating that ion **3** is only a noncontributing higher lying intermediate. Below −120 °C, ion **1** tends to precipitate out of the acid solution, hindering further lower temperature studies. One can estimate an upper limit of 5 kcal/mol for the barrier of equilibration. Ion **1** at −40 °C irreversibly rearranges to the 2,3-dimethylbutenyl cation **4**. The ^{13}C chemical shifts of **4** are δ 272.4 (singlet), 170.8 (triplet), 154.8 (singlet), 37.3, 34.3, and 17.8 (quartets). The formation of **4** can be readily rationalized by a deprotonation–ionization mechanism.



4

The present study shows that there is no evidence for a fluorine shift, and consequently involvement of bridged tetramethylethylenefluoronium ion either as an intermediate or a transition state is clearly ruled out in the equilibration of the 2,3-dimethyl-3-fluoro-2-butyl cation **1** in superacid solution.

We know of no evidence for fluoronium ions in solution chemistry. Attempted acid-catalyzed isomerization of fluoroaromatics, including *o*-difluorobenzene, was unsuccessful,[8] again indicating the resistance of fluorine to participate in bridging with adjacent electrophilic centers, which would place partial positive charge on the fluorine. This is in contrast to electrophilic fluorination[9] with polarized or complexed elementary fluorine, where the weak F–F bond is sufficiently polarizable to allow electrophilic character on fluorine but certainly not formation of a positive fluorine ion.

Experimental Section

2,3-Difluoro-2,3-dimethylbutane was prepared from 2,3-dimethyl-2-butene as described.[6,10]

Preparation of the Ion. The difluoro precursor, dissolved in SO_2ClF precooled at −78 °C (dry ice/acetone bath), was slowly added with vigorous stirring to a freshly prepared solution of SbF_5/SO_2ClF at −90 °C (ethanol/liquid N_2 slush) in a 10-mm NMR tube so as to obtain an approximately 10–15% solution of the ion.

The ^{13}C NMR spectra were obtained on a Varian Associates Model FT-80 spectrometer equipped with a variable-temperature broad-band probe. The ^{13}C NMR chemical shifts are in part per million from external capillary tetramethylsilane.

Acknowledgment. Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

Registry No. 1, 53172-48-8; 2, 53172-53-5; 3, 53172-41-1; 4, 71983-43-2; 2,3-difluoro-2,3-dimethylbutane, 17603-29-1.

---

[7] Clark, D. T. In "Special Lectures of the 23rd International Congress of Pure and Applied Chemistry", Boston, 1971; Butterworth: London, Vol. 1, p 31.

[8] Olah, G. A., Schleyer, P. v. R., Eds. In "Carbonium Ions"; Wiley Interscience: New York, 1976; Vol. V, p 2207.

[9] (a) Barton, D. H. R.; Hesse, R. H.; Markwell, R. E.; Pechet, M. M.; Toh, H. T. *J. Am. Chem. Soc.* **1976**, *98*, 3034. (b) Lerman, O.; Rozen, S. *J. Org. Chem.* **1983**, *48*, 724 and references cited therein. (c) Rozen, S., unpublished results.

[10] Olah, G. A.; Welch, J. T.; Vankar, Y. D.; Nojima, M.; Kerekes, I.; Olah, J. A. *J. Org. Chem.* **1979**, *44*, 3872.

"Anti-Hammond" Transition-State Structural Variation in the Context of Marcus' Rate Theory

Joseph L. Kurz

Department of Chemistry, Washington University, St. Louis, Missouri 63130

Received May 3, 1983

Marcus' rate equation has been shown to be quite useful in the description of atom-transfer and group-transfer reactions,[1] even though it originally[2] was derived from a model for outer-sphere electron transfer. For example, it has been applied extensively to analyses of substituent and isotope effects on proton transfer[3] and has been used to correlate rates of methyl transfers in aqueous solution.[4]

Such general applicability is to be expected, since the form of Marcus' rate equation results from the widely valid

---

[1] For a critical review of applications of Marcus' rate theory, see: Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227–263.

[2] Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679–701, and earlier papers cited therein.

[3] For example: (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891–899. (b) Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475–503. (c) Kresge, A. J. In "Isotope Effects on Enzyme-Catalyzed Reactions"; Cleland, W. W., O'Leary, M. H., Northrup, D. B., Eds.; University Park Press: Baltimore, 1977; pp 37–63. (d) Kreevoy, M. M. In "Isotopes in Organic Chemistry"; Buncel, E., Lee, C. C., Eds.; Elsvier: Amsterdam, 1976; Vol. 2; pp 1–31.

[4] Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87–157.

0022-3263/83/1948-5117$01.50/0

approximation that all contributions to the free energy barrier vary as the square of the fractional displacement along the reaction coordinate.[5,6] Moreover, the common depiction of the barrier in terms of two intersecting parabolae (which was natural for outer-sphere electron transfer) can be shown[5] to be exactly equivalent to its depiction as a smooth inverted parabolic barrier (which corresponds more closely to the smooth barriers commonly drawn for atom-transfer and group-transfer reactions). For emphasis of this equivalence, the figures illustrating the following discussion show barriers *both* in terms of intersecting parabolae (dashed curves) and as the corresponding equivalent smooth barrier (solid curves).

One problem that arises in such applications of Marcus' rate theory is that of accommodating what has been called[7] "Anti-Hammond" behavior of transition-state structures. Currently accepted descriptions of transition-state structural variations in terms of perturbations of free energy surfaces[8] lead to the expectation that changes in reactant structure which increase the rate of a reaction almost always will make the transition state "earlier" in the sense of being more "reactant-like". In the following discussion, reaction series in which the transition-state structure behaves in this way will be said to exhibit "Hammond" behavior, while reaction series in which the faster reactions have more product-like transition states will be said to exhibit "anti-Hammond" behavior.[9] Reactions the structures of whose transition states vary in the Hammond manner are expected to obey the reactivity–selectivity principle,[11] and, as is shown below, Hammond behavior is predicted by Marcus' rate theory for almost all cases.

An Example of Anti-Hammond Behavior. Alkyl-transfer reactions provide several examples of sets of apparently simple reactions for which violations of the reactivity–selectivity principle and other indicators of anti-Hammond behavior are well documented.[7,11-16] Consider in particular the observed[16] $^{14}N/^{15}N$ kinetic isotope effects on methyl transfer (eq 1) from *p*-toluenesulfonate ($X^- = OTs^-$) and trifluoromethanesulfonate ($X^- = OTf^-$) to substituted pyridines. These isotope effects are indicators of the extents of N–C bonding in the transition state, and the observed values of k_{14}/k_{15} imply that the N–C bond order in the transition state is larger for transfer from OTf^- than for transfer from OTs^-. Since the reactions of CH_3OTf are ca. 10^4 times faster than those of CH_3OTs, this implication is contrary to predictions based on free energy surface perturbations.[8]

$$N + CH_3X \rightarrow {}^+NCH_3 + X^- \qquad (1)$$

Application of Conventional Marcus' Theory. According to Marcus' theory,[17] the observed standard free energy barrier, $\Delta G_{NX}^{\ddagger}$, for the transfer of CH_3^+ from X^- to N (eq 1) is related to the overall standard free energy change, $\Delta G°$, and to the observable (at least in principle) values of $\Delta G_{NN}^{\ddagger}$ and $\Delta G_{XX}^{\ddagger}$ for the corresponding symmetric transfers (eq 2 and 3, respectively) by eq 4, where

$$N + CH_3N^+ \rightarrow {}^+NCH_3 + N \qquad (2)$$

$$X^- + CH_3 \rightarrow XCH_3 + X^- \qquad (3)$$

$$\Delta G_{NX}^{\ddagger} = \Delta G_{int}^{\ddagger}(1 + \Delta G_{NX}°/4\Delta G_{int}^{\ddagger})^2 \qquad (4)$$

the intrinsic barrier, $\Delta G_{int}^{\ddagger}$, is the arithmetic mean of $\Delta G_{NN}^{\ddagger}$ and $\Delta G_{XX}^{\ddagger}$ (eq 5). If the reaction coordinate is denoted by z ($z = 0$ and 1 for reactants and products, respectively), then $z_{\ddagger}$, the fractional displacement of the transition state along the reaction coordinate can be shown[5] to be given by eq 6.

$$\Delta G_{int}^{\ddagger} = \frac{1}{2}(\Delta G_{NN}^{\ddagger} + \Delta G_{XX}^{\ddagger}) \qquad (5)$$

$$z_{\ddagger} = \frac{1}{2}(1 + \Delta G_{NX}°/4\Delta G_{int}^{\ddagger}) \qquad (6)$$

Suppose that the leaving group X^- is changed to a faster leaving group, Y^-. Equation 4 shows that the rate increase ($\Delta G_{NY}^{\ddagger} < \Delta G_{NX}^{\ddagger}$) can arise from two sources, a shift of the equilibrium toward product ($\Delta G_{NY}° < \Delta G_{NX}°$) and/or a lowering of the intrinsic barrier, $\Delta G_{int}^{\ddagger}$ (i.e., from $\Delta G_{YY}^{\ddagger} < \Delta G_{XX}^{\ddagger}$ in eq 5).[18] Similarly, eq 6 shows that the location of the transition state, $z_{\ddagger}$, also will change by an amount that depends on those same two variables. A decrease in $\Delta G°$ always will tend both to increase the rate (decrease $\Delta G^{\ddagger}$) and to make the transition state earlier (decrease $z_{\ddagger}$); this is *Hammond* behavior. In contrast, although a decrease in $\Delta G_{int}^{\ddagger}$ always will tend to increase the rate, its effect on $z_{\ddagger}$ depends on the sign of $\Delta G°$; when $\Delta G° < 0$ it will tend to decrease $z_{\ddagger}$ (*Hammond* behavior), and when $\Delta G° > 0$ it will tend to increase $z_{\ddagger}$ (*anti-Hammond* behavior).

The above conclusions can be made quantitative by differentiating eq 4 and 6 to give eq 7 and 8. In eq 7 the

$$d\Delta G^{\ddagger} = z_{\ddagger}d\Delta G° + 4z_{\ddagger}(1 - z_{\ddagger})d\Delta G_{int}^{\ddagger} \qquad (7)$$

$$dz_{\ddagger} = \left(z_{\ddagger} - \frac{1}{2}\right)(d\Delta G°/\Delta G° - d\Delta G_{int}^{\ddagger}/\Delta G_{int}^{\ddagger}) \qquad (8)$$

coefficients of both $d\Delta G°$ and $d\Delta G_{int}^{\ddagger}$ are always positive, while in eq 8 the coefficient of $d\Delta G_{int}^{\ddagger}$ is positive when $\Delta G° < 0$ (and $z_{\ddagger} < {}^1/_2$) and negative when $\Delta G° > 0$ (and $z_{\ddagger} > {}^1/_2$). Since anti-Hammond behavior corresponds to the

---

(5) Kurz, J. L. *Chem. Phys. Lett.* **1978**, *57*, 243–246.

(6) Reference 1, p 228.

(7) Pross, A.; Shaik, S. S. *J. Am.* Chem. *Soc.* **1981**, *103*, 3702–3709.

(8) For example: (a) Harris, J. C.; Kurz, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 349–355. (b) Harris, J. M.; Shafer, S. G.; Moffat, J. R.; Becker, A. R. *Ibid.* **1979**, *101*, 3295–3300. (c) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.,; Harper & Row: New York, 1981; Chapters 2 and 4.

(9) Marcus' rate theory describes the reaction coordinate in terms of a single displacement variable (vide infra). Thus, characterization of a transition state as "early" or "late" appears unambiguous from the point of view of Marcus' theory. However, if a reaction involves two or more processes that may be asychronous (e.g., bond making, bond breaking, and solvent repolarization during an alkyl transfer), the transition state could be late with respect to one process and early with respect to another. Free energy surface perturbtion models for transition-state structural variation describe differences between the extents of such asynchronies in terms of displacements parallel and perpendicular to the reaction coordinate.[8] In conventional Marcus' theory, the effects of perpendicular displacements on the barrier height can be accommodated only by changes in the intrinsic barrier.[10] The modification of Marcus' theory proposed below in this discussion can be viewed as an alternative approach that accommodates large asychronies more satisfactorily than does the conventional estimation of the intrinsic barrier as the mean of the barrier in the corresponding symmetric reactions.

(10) Murdoch, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 2159.

(11) For reviews of the reactivity–selectivity principle, see: (a) Pross, A, *Adv. Phys. Org. Chem.* **1977**, *14*, 69–126. (b) Johnson, C. D. *Chem. Rev.* **1975**, *75*, 755–765.

(12) Westaway, K. C.; Ali, S. F. *Can. J. Chem.* **1979**, *57*, 1354–1367.

(13) Ballistreri, F. P.; Maccarone, E.; Mamo, A. *J. Org. Chem.* **1976**, *41*, 3364–3367.

(14) Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892–5902.

(15) Grimsrud, E. P.; Taylor, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 739–741.

(16) Kurz, J. L.; Seif El-Nasr, M. M. *J. M. Chem. Soc.* **1982**, *104*, 5823–5824.

(17) In the following discussion we are neglecting the work terms w^r and w^p for formation of the precursor and successor complexes from free reactants and free products, respectively. For reactions of this charge type, w^r and its sensitivity to the isotopic identity of the pyridine nitrogn should both be small and w^p should not be sensitive to the isotopic identity of the nitrogen. We also are assuming that desolvation contributions to w^p are not sufficiently different for OTs^- and OTf^- to control the difference in transition-state structure.

(18) For a more detailed discussion of this point, see ref 1, p 233.

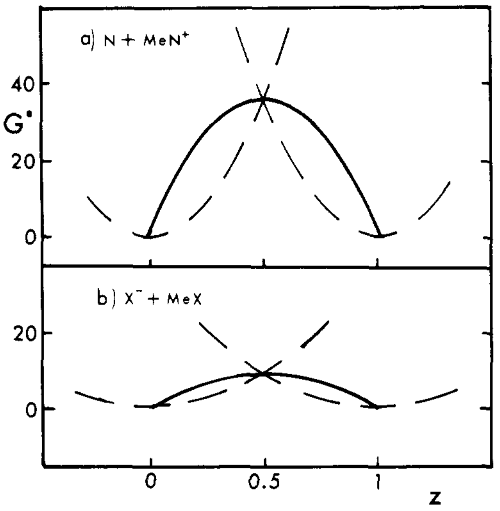


Figure 1. Barriers for the corresponding symmetric methyl transfers. These barriers are used in the construction of Figures 2 and 3. In a, $\Delta G_{NN}^{\ddagger} = 36$; in b, $\Delta G_{XX}^{\ddagger} = 9$ (units are arbitrary).

coefficients of $dz_{\ddagger}$ and $d\Delta G^{\ddagger}$ having opposite signs, eq 7 and 8 thus show that such behavior requires both

$$\Delta G^{\circ} > 0 \qquad (9a)$$

and

$$d\Delta G_{int}^{\ddagger}/\Delta G_{int}^{\ddagger} > d\Delta G^{\circ}/\Delta G^{\circ} \qquad (9b)$$

Since the displacements of OTs⁻ and OTf⁻ by pyridine bases have $\Delta G^{\circ} < 0$ (they go to completion), the observed behavior of the $^{14}N/^{15}N$ kinetic isotope effects cannot be accounted for in terms of conventional Marcus' theory. Even for reactions that are thermodynamically "uphill" (i.e., with $\Delta G^{\circ} > 0$), eq 9b is quite restrictive; it requires that the fractional increase in $\Delta G_{int}^{\ddagger}$ must exceed that in ΔG° in order for anti-Hammond behavior to result, and since varying the structure of one reactant changes only one of the corresponding symmetric reactions, eq 5 requires that the fractional change in $\Delta G^{\ddagger}$ for that symmetric reaction be more than *twice* that in ΔG°.

A Modification of Marcus' Theory. A simple modification allows Marcus's theory to accommodate anti-Hammond behavior in reactions with either sign of ΔG°. Conventional Marcus' theory approximates the intrinsic barrier by averaging the intrinsic barriers for the corresponding symmetric reactions (eq 5). This is equivalent to averaging the force constants for the NN and XX parabolae to estimate the force constant for the NX parabola (see Figure 2, curve a). This averaging is reasonable if the changes in the N–CH_3 and CH_3–X bond order during the activation process are approximately synchronous and equal in magnitude but is *not* reasonable if the contributions of those bonding processes to the barrier are asynchronous.

For example, suppose that the ability of the trifluoromethanesulfonate moiety to accommodate and stabilize a negative charge is sufficient to cause the transition state to have a structure in which CH_3–OTf bond breaking is more advanced[19] than is N–CH_3 bond making, then motion along that part of the reaction coordinate which is near the reactants would be largely a change in CH_3–X bonding while motion along that part of the reaction coordinate which is near the products would be largely a change in N–CH_3 bonding, and the reaction profile could be approximated by the unaveraged XX parabola near the reactants and by the unaveraged NN parabola near the products.

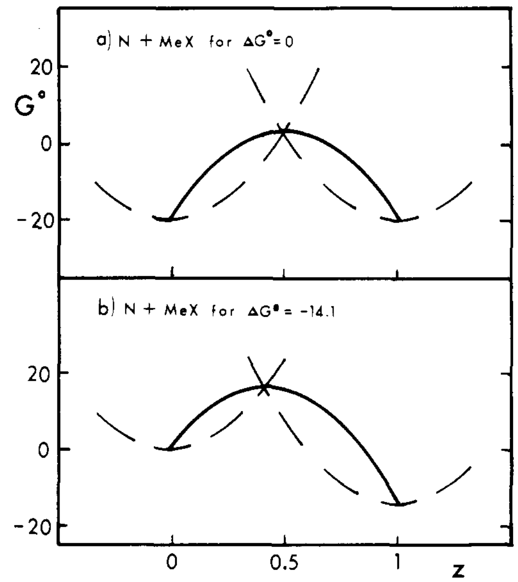


Figure 2. *An illustration of the construction of the barrier for* N + MeX according to conventional Marcus' theory. The barriers shown in Figure 1 are the basis of this construction. (a) The intrinsic barrier, for which $\Delta G^{\circ} = 0$, $z_{\ddagger} = 0.50$, and $\Delta G^{\ddagger} = \Delta G_{int}^{\ddagger} = {}^{1}/_{2}(\Delta G_{NN}^{\ddagger} + \Delta G_{XX}^{\ddagger}) = 22.5$. (b) The result of decreasing ΔG° to -14.1 while $\Delta G_{int}^{\ddagger}$ remains 22.5: $z_{\ddagger}$ decreases from 0.50 to 0.42 and $\Delta G^{\ddagger}$ decreases from 22.5 to 16. This is Hammond behavior.

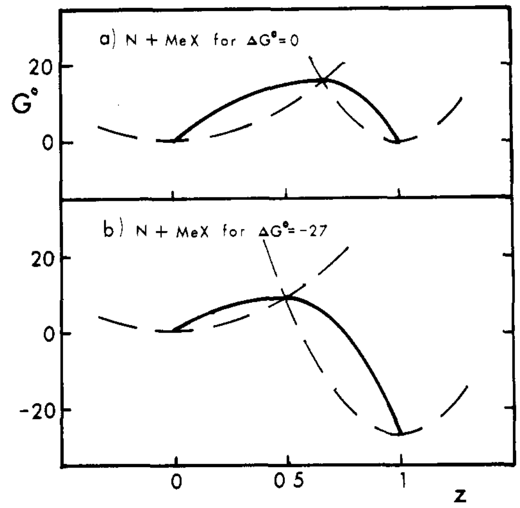


Figure 3. An illustration of the construction of an unsymmetric barrier for N + MeX by the direct use of the unaveraged barriers for N + MeN⁺ and X⁻ + MeX shown in Figure 1. (a) The resulting barrier when ΔG° remains zero (the analogue of the intrinsic barrier in conventional Marcus' theory). If this barrier is regarded as being derived from that for N + MeN⁺ (Figure 1a) by changing the leaving group from N to X⁻, then it illustrates the origin of anti-Hammond behavior in this model ($z_{\ddagger}$ increases from 0.50 to 0.67 while $\Delta G^{\ddagger}$ decreases from 36 to 16). (b) An illustration of the opposing Hammond effect that can arise from a decrease in ΔG°. Comparison to Figure 3a illustrates how large the decrease in ΔG° must be in order for this Hammond effect to be dominant over the anti-Hammond structural effect that results from the use of unaveraged barriers; to keep $z_{\ddagger} \le 0.50$, $\Delta G^{\ddagger}$ must be reduced to ≤ 9 (the value of $\Delta G_{XX}^{\ddagger}$), which requires $\Delta G^{\circ} \le -27$.

Such an approximation of the barrier shape by the unaveraged parabolae generates anti-Hammond changes in $z_{\ddagger}$. This is illustrated in Figure 3. Figure 2 illustrates how an observed $\Delta G^{\ddagger}$ of 16 arbitrary units could be generated via conventional Marcus' theory from symmetric reactions with $\Delta G_{NN}^{\ddagger} = 36$ $\Delta G_{XX}^{\ddagger} = 9$; comparison of Figure 2, a and b, demonstrates how decreasing ΔG° de-

---

[19] Perhaps for reasons related to those suggested in ref 7.

creases $\Delta G^\ddagger$ and also *decreases* $z_\ddagger$; this is Hammond behavior. In contrast, Figure 3a shows how the same value of $\Delta G^\ddagger$ (16) can be obtained from the same values of $\Delta G_{NN}^\ddagger$ and $\Delta G_{XX}^\ddagger$ without averaging them to obtain $\Delta G_{int}^\ddagger$; comparison of Figures 1a and 3a demonstrates how replacing the NN reactant parabola with the more gently curved XX parabola while retaining the NN product parabola decreases $\Delta G^\ddagger$ and also *increases* $z_\ddagger$; this is anti-Hammond behavior.

In addition to this direct anti-Hammond effect, if the change in the reactant parabola is accompanied by a change in ΔG°, then that variation in ΔG° can result in an opposing Hammond effect. Figure 3b illustrates how large a decrease in ΔG° would have to be in order for its tendency to decrease $z_\ddagger$ to be dominant.

Conclusions

Marcus' rate theory in its conventional form is unable to accommodate anti-Hammond transition-state structural variation in reactions for which $\Delta G^\circ < 0$. One way to extend Marcus' theory to allow it to be consistent with such behavior is to modify the usual assumption that $\Delta G_{int}^\ddagger$ is the mean of the two $\Delta G^\ddagger$ values for the corresponding symmetric reactions. That assumption is expected to be valid for reactions in which bond breaking and bond making occur synchronously and to equal extents; it should not be valid if those two processes are not in step with one another, and in the limit of complete asynchrony the barrier would be correctly modeled by two intersecting parabolae: one with it force constant equal to that of the bond being broken and the other with its force constant equal to that of the bond being formed. This mode of barrier construction allows anti-Hammond behavior.

Thus, conversely, observations that imply anti-Hammond behavior may be diagnostic of the presence of such an asynchrony. Similar conclusions recently have been reached by other investigators[20-22] via arguments that do not directly involve Marcus' theory. It will be interesting to see whether the surprising implication of such conclusions that even *methyl* transfers can have significant asychrony turns out to be correct.

Acknowledgment. This work was supported in part by Grant CHE83-04874 from the National Science Foundation.

---

[20] Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1129–1130.

[21] Buncel, E.; Wilson, H.; Chuaqui, C. *J. Am. Chem. Soc.* **1982**, *104*, 4896–4900.

[22] Giese, B. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 125–136.

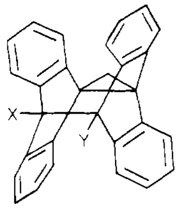
Synthesis and Chemistry of an Unusual Bridgehead Alkene

Joan Zitzmann Suits, Douglas E. Applequist,* and
Daniel J. Swart

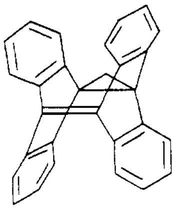
Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Received July 6, 1983

We previously described the preparation of bromide **1a** from photocyclization of (9-bromoanthryl)anthrylmethane,[1] and we also gave a preliminary indication of the dehydrobromination of **1a** to form the bridgehead alkene **2** using the Greene procedure[2] of capture of **2** with azide ion and subsequent amination and oxidation of the resulting triazoline. The preliminary result has now been confirmed and the identity of **2** established by its chemistry and single-crystal X-ray diffraction. The X-ray study gave limited information because the crystals were disordered, with the alkene and cyclopropane units randomly interchanged so that only a mean bridgehead–bridgehead bond distance (1.595 Å) could be determined.

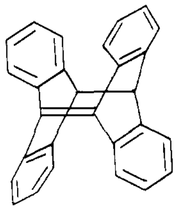


1a, X = Br; Y = H
b, X = I; Y = I
c, X = CH_3; Y = H



2

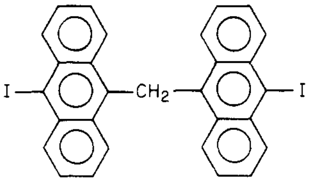
Compound **2** is interesting particularly because of the possibility that the uniquely positioned alkene and cyclopropane rings might interact to affect the rates or products of chemical reactions. The X-ray study showed the double bond carbons and the opposite cyclopropane carbons to be separated by 2.661 Å. Of special value as a model is the simple dehydrodianthracene **3**, prepared earlier by Greene and co-workers.[2,3] The preparation of **3** has been repeated in order to make comparisons.



3

Compound **2** has been found to be qualitatively and quantitatively more reactive than **3**. The reactions discovered for **2** have been reactions of the alkene function only, however, with no transannular participation by the cyclopropane ring in product formation. Iodine, oxygen, and HBr all add to **2** but not to **3**.

The reaction of **2** with I_2 in carbon tetrachloride yields bis(10-iodoanthryl)methane (**4**), in a process markedly accelerated by light and inhibited by isoamyl nitrite. A free-radical chain mechanism is inferred, and a probable intermediate is the bridgehead diiodo compound **1b**. Chlorine and bromine add to **2** to give analogous products.



4

The reaction of **2** with oxygen can be carried out by bubbling oxygen through a carbon tetrachloride solution of **2** at room temperature. The first product is a colorless 1:1 adduct with a mass spectral parent mass at 398 and shows no carbonyl stretching bands in the infrared. The

---

[1] Applequist, D. E.; Swart, D. J. *J. Org. Chem.* **1975**, *40*, 1800.

[2] Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 4342.

[3] Weinshenker, N. M.; and Greene, F. D. *J. Am. Chem. Soc.* **1968**, *90*, 506.