size of the trapped radical influences this angle, the difference in $A_{\beta H}$ is probably due to the steric requirements of $CoSMDPT-O_2$. Clearly, we have obtained further support for our earlier conclusions about cobalt(II) coordination enhancing the basicity and reactivity of molecular oxygen.

Steric Inhibition of Hyperconjugation. Vanishing Equilibrium Isotope Effect in Bridgehead-Deuterated 2,3-Dimethylbicyclo[2.2.2]octyl Cation

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Secondary isotope effects on reaction rates arise from force-field changes at the isotopic position between the reactant and the transition state.[1] A significant array of experimental results indicate that hyperconjugation makes at least the dominant if not the sole contribution to the β-deuterium isotope effect in carbenium ion solvolysis reactions.[2] Shiner[3] furnished the first data relating the dihedral angle between an adjacent C–H or C–D bond and the vacant p orbital of the cation center with the magnitude of the isotope effect. The magnitude of kinetic isotope effects in solvolysis may be distorted by possible multiple reaction pathways like competing elimination, participation, ion pairing, rearrangements, and other factors.[4] Equilibrium isotope effects in degenerate rearrangements of stable carbocations involve only the properties of well-defined species that can be measured by NMR spectroscopy.[5]

We have investigated the angular dependence of the β-deuterium equilibrium isotope effect in a stable model cation with fixed stereochemistry to prove the hyperconjugational origin unambigiously.

The 2,3-bicyclo[2.2.2]octyl cation **1** combines both prerequisites, a fast degenerate 2,3-hydride shift **1a** ⇌ **1b**, which might be perturbed by β-deuterium, and a fixed dihedral angle of 90° between the vacant p orbital of the cation center and the C–D bond in the bridgehead-deuterated cation **3**. The methyl-deuterated cation **2**, which should show a conformation-independent isotope effect,[6] can serve as a model for the other limiting conformation with a dihedral angle of 0°.

Solutions of **1** in SO_2ClF/SO_2F_2 were prepared from the corresponding chloride[7] by reaction with SbF_5 using standard methods.[8] At −122 °C the ^{13}C NMR spectrum of **1** (Figure 1a)[9]
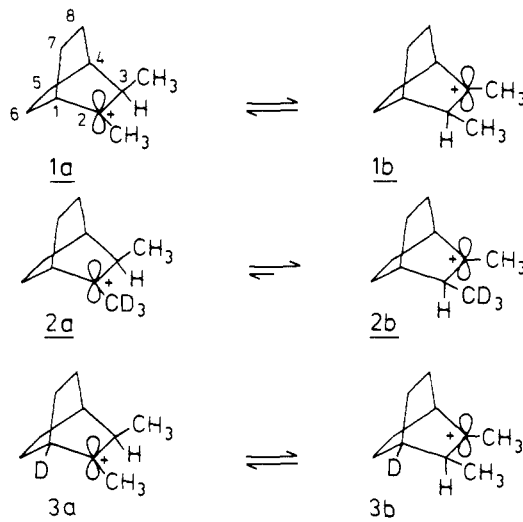
shows four peaks (56.12 ppm averaged bridgehead carbons C_1, C_4; 29.43 ppm averaged methylene carbons C_7, C_8 endo to CH_3; 24.98 ppm averaged methyl carbons; 23.78 ppm averaged methylene carbons C_5, C_6 exo to CH_3). The peak of the averaged cation and methine carbons C_2 and C_3 is not observable due to very large kinetic line broadening at these conditions. Assignments were made from different temperature-dependent line broadening and ^1H-coupled and ^1H-specific-decoupled ^{13}C NMR spectra and were confirmed by analysis of the ^{13}C NMR spectra of the deuterated cations **2** and **3**. The time-averaged symmetry in the spectrum proves the fast 2,3-hydride shift in cation **1a** ⇌ **1b**. The energy barrier for the 2,3-hydride shift was determined as $\Delta G^{\ddagger}$ = 4.7 ± 0.15 kcal/mol[10] at −122 °C.

Cation **2** was prepared analoguously to **1** from 2-chloro-2-(trideuteriomethyl)-3-methylbicyclo[2.2.2]octane.[7] The ^{13}C NMR spectrum (Figure 1b) shows typical splittings of the averaged peaks due to the lifting of the degeneracy of the equilibrium **1a** ⇌ **1b**. As expected the largest isotope splittings are observed for those signals showing the largest kinetic line broadening. At −122 °C the bridgehead-carbon signals are split into two peaks by 6.6 ppm, the C_7, C_8 carbons by 4.4 ppm, and the C_5, C_6 carbons by 0.3 ppm. The isotope splitting of the CH_3/CD_3 groups is 6.4 ppm. The upfield peak is of lower intensity because of extra broadening due to unresolved deuterium coupling, longer relaxation time, and unfavorable NOE. The upfield shift of the CD_3 peak is 0.9 ppm larger than the downfield shift of the CH_3 peak. This shows the direction of the isotope effect. The CD_3 peak at higher field means the isomeric cation with the CD_3 group further removed from the positive charge, i.e., **2b**, is favored in the equilibrium **2a** ⇌ **2b**.

Hyperconjugative stabilization of the positive charge decreases the force constants of the C–H bonds in the adjacent methyl group. The zero point energy of this methyl group is lower than that at the remote position. A CH_3 group has a priori a higher zero point energy than a CD_3 group, thus CH_3 is lowered more in energy when attached adjacent to the charged carbon, hence the equilibrium **2a** ⇌ **2b** is shifted toward **2b**. The size of the equilibrium constant is calculated from the isotope splitting. Using the equation[5] $K = (\Delta + \delta)/(\Delta - \delta)$ we obtain K_{CD_3} = 1.73 at −120 °C.

Equilibrium isotope effects and thus the isotope splittings δ are temperature dependent.[2] ln K was found to vary lineary with $1/T$ in the temperature region studied (−137 to −92 °C). The thermodynamic parameters for the equilibrium **2a** ⇌ **2b** were determined from ln $K = -\Delta H/(RT) + (\Delta S/R)$ via regression analysis as ΔH = 65 ± 2.5 cal/mol per D and ΔS = 0.06 ± 0.007

(1) Wolfsberg, M.; Stern, M. J. *Pure Appl. Chem.* **1964**, *8*, 325.
(2) Collins, C. J., Bowman, N. S. Eds. "Isotope Effects in Chemical Reactions"; van Nostrand Reinhold: New York, 1970.
(3) (a) Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 265. (b) Shiner, V. J., Jr.; Humphrey, J. S., Jr. *Ibid.* **1963**, *85*, 2416.
(4) See, for example: Shiner, V. J., Jr.; Neumann, T. E.; Fischer, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 354.
(5) (a) Saunders, M.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2259 and 2561. (b) Saunders, M.; Telkowsky, L. A.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070.
(6) Sunko, D. E.; Szele, I.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 5000.
(7) Synthetic procedures will be reported in a full paper.
(8) Saunders, M.; Cox, D.; Lloyd, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 6656.

(9) Cations **1–3** are in equilibrium with two isomeric dimethylbicyclo-[3.2.1]octyl cations at higher temperatures. Details will be reported in a full paper.
(10) Chemical-shift differences Δ for a static cation **1a** were estimated by using 2-methylbicyclo[2.2.2]octyl cation[11] as a model compound.
(11) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1978**, *100*, 1487.
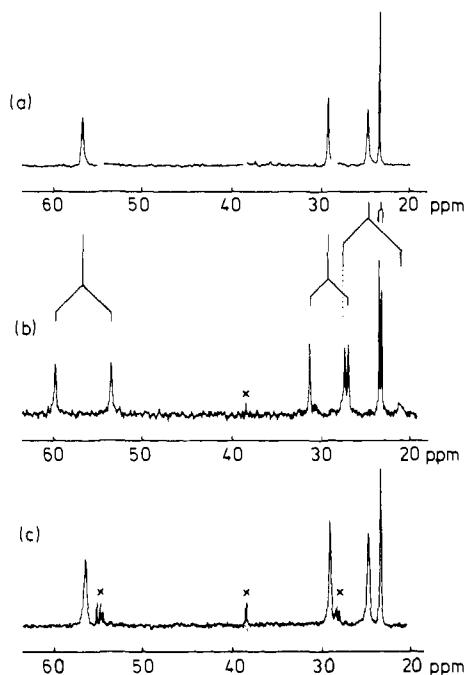(12) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8071.

Figure 1. (a–c) 100.6-MHz ^{13}C NMR spectra of cations 1–3 in SO$_2$ClF/SO$_2$F$_2$ at –122 °C. Peaks marked (x)[9] are deleted in the upper trace.

cal/degree per D. These values are in good agreement with those reported for other equilibrating carbocations.[5] They are also very similar to the $\Delta\Delta F^{\ddagger}$ values reported[13] for β-secondary kinetic isotope effects in solvolysis of alkyl halides which proceed via trigonal carbonium ion intermediates.

Cation 3 was prepared from the reaction of 2-chloro-2,3-dimethyl-4-deuteriobicyclo[2.2.2]octane[7] with SbF$_5$. The ^{13}C NMR spectrum (Figure 1c) measured at –123 °C shows only four kinetically broadened signals. As in 1 and 2, in 3 the peak of the averaged C$^+$/CH carbons is not visible. In contrast to the spectra of 2 the spectra of 3 do not show any sizeable splittings, thus the spectra of 1 and 3 are very similar. Very small splittings may be buried under the broad lines. The broadest peak, i.e., the averaged C$_1$, C$_4$ peak, has a line width of 42 Hz at –122 °C, which yields a calculated maximum for $K = 1.03$ per D.

Small temperature-independent splittings (0.106 ppm) are observed for the averaged C$_5$, C$_6$ peak, which shows the smallest kinetic line broadening. This splittings are most likely due to intrinsic isotope shifts.[14] The absence of equilibrium isotope splittings in 3 is confirmed by the ^{1}H NMR spectrum, which is virtually identical with that of cation 1 except the peak of the bridgehead protons having only half the intensity.

We interpret these results as a direct proof for the hyperconjugational origin of the equilibrium isotope effect. In 2 maximum overlap between the vacant p orbital and one of the methyl C–D (2a) C–H bonds (2b) is always possible leading to large equilibrium isotope splittings. In 3 the dihedral angle of 90° permits no overlap of the vacant p orbital with the bridgehead C–D (3a) or C–H (3b) bond; hence no equilibrium isotope splittings are observed. In valence bond terminology the hyperconjugation in 3 is sterically suppressed because the "no bond" resonance structure would be a bridgehead olefin and thus too unstable to contribute significantly to the hyperconjugational stabilization of the cation.

These results obtained on stable ions give important evidence for the concept of steric inhibition of hyperconjugation of a given CH bond in carbocations. They support the interpretation of solvolysis rates of comparable deuterated bicyclic systems[15] and

(13) Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 240. Servis, K. L.; Borcic, S.; Sunko, D. E. *Tetrahedron* **1968**, *24*, 1247.

(14) The intrinsic isotope shifts in 3-OH are 0.11 ppm for the adjacent carbons and 0.03 ppm for the remote carbons.

(15) (a) Reference 3. (b) Maskill, H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1889.

are in agreement with isotope effects theory and recent ab initio calculations.[16]

(16) DeFrees, D. J.; Hehre, W. J.; Sunko, D. E. *J. Am. Chem. Soc.* **1979**, *101*, 2323.

On the Application of the Marcus Equation to Methyl Transfer (S$_N$2) Reactions

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The Marcus equation (1) was originally developed to model electron transfer reactions.[1] It was soon extended to the analysis

$$\Delta G^* = ((\Delta G°)^2/16\Delta G_o^*) + \Delta G_o^* + \tfrac{1}{2}\Delta G° \qquad (1a)$$

$$\alpha = d\Delta G^*/d\Delta G° = \tfrac{1}{2} + (\Delta G°/8\Delta G_o^*) \qquad (1b)$$

of proton and atom transfer reactions,[2] however, and more recently to methyl group transfer (S$_N$2) reactions in the gas phase[3] and in solution.[4] In addition, the theory has been applied to barriers determined by ab initio calculations.[5] Herein we report kinetic results that satisfy an exacting test of the legitimacy of the Marcus equation with regard to methyl group transfer; we find that values of α derived from the Marcus equation correctly predict the slope of a Bronsted-type (Hammett) plot. ($\Delta G°$, ΔG^*, and ΔG_o^* are the free energies of reaction, activation, and "intrinsic" activation, respectively.)

On the basis of Marcus's original derivation,[1] which assumes zero overlap between the electronic orbitals of the reactant molecules in the activated complex, one might not expect success of the equation in applications to proton, let alone methyl group, transfers. However, other approaches have been employed to derive the same, or a similar, equation.[6] Prominent among these is Murdoch's method, which assumes only a linear free energy relationship,[7] a condition widely satisfied in group transfer reactions. One of the most powerful implications is the identification of the Marcus α with the slope of Bronsted correlations. Consequently, by measuring ΔG^* and $\Delta G°$ for single reaction and using the Marcus equation (1a), one can predict the activation energies (and thus the rates) for any number of closely related reactions, such as those in which a substituent is changed.[8] Indeed, the remarkable predictive power of (1a) has been demonstrated for several groups of proton and atom transfer reactions.[2]

Gas-phase kinetic studies were performed on a series of substituted benzyl anions reacting with methyl bromide in a pulsed ion cyclotron resonance spectrometer.[9,10] Bimolecular rate

(1) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196.

(2) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891–899. (b) Cohen, A. O.; Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 4249–4256.

(3) (a) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993–5999. (b) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 2672–2680.

(4) (a) Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227–263. (b) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87–158. (c) Lewis, E. S.; Kukes, S.; Slater, C. D. *J. Am. Chem. Soc.* **1980**, *102*, 1619–1623.

(5) (a) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7692–7694. (b) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7694–7696 and references therein.

(6) Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475–503.

(7) (a) Murdoch, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 4410–4418. (b) Murdoch, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 2159–2164.

(8) Provided ΔG_o^* is constant throughout the series; see: Marcus, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 7224–7225 and ref 4.

(9) (a) McIver, R. T., Jr. *Rev. Sci. Instrum.* **1978**, *49*, 111–118. (b) McIver, R. T.; Jr.; Hunter, R. L.; Ledford, E. B., Jr.; Locke, M. J.; Francl, T. J. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 65–84.