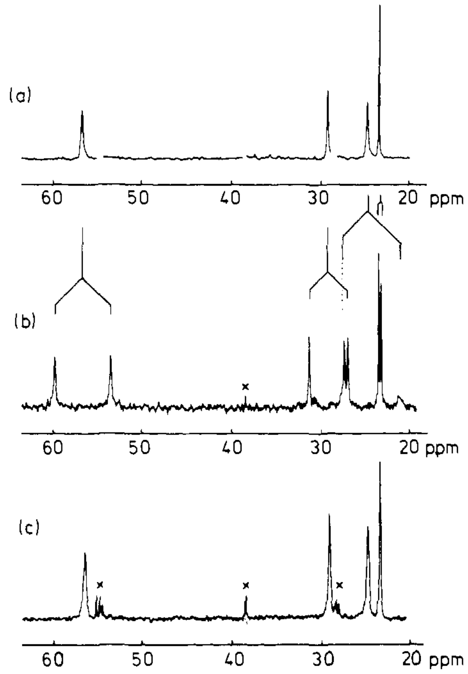

Figure 1. (a–c) 100.6-MHz ^{13}C NMR spectra of cations **1–3** in SO_2ClF/SO_2F_2 at −122 °C. Peaks marked (x)[9] are deleted in the upper trace.

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 $\Delta\Delta F^*$ 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 ^1H 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 are in agreement with isotope effects theory and recent ab initio calculations.[16]

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On the Application of the Marcus Equation to Methyl Transfer (S_N2) Reactions

James A. Dodd and John I. Brauman*

Department of Chemistry, Stanford University
Stanford, California 94305

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

$$\Delta G^* = ((\Delta G^\circ)^2/16\Delta G_0^*) + \Delta G_0^* + \tfrac{1}{2}\Delta G^\circ \qquad (1a)$$

$$\alpha = d\Delta G^*/d\Delta G^\circ = \tfrac{1}{2} + (\Delta G^\circ/8\Delta G_0^*) \qquad (1b)$$

of proton and atom transfer reactions,[2] however, and more recently to methyl group transfer (S_N2) 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. (ΔG°, ΔG^*, and ΔG_0^* 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 Brønsted correlations. Consequently, by measuring ΔG^* and ΔG° 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

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[8] Provided ΔG_0^* is constant throughout the series; see: Marcus, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 7224–7225 and ref 4.

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Table I. Bimolecular Rate Constants, Efficiencies, Energies,[a] and α's for $ArCH_2^- + CH_3Br$

substituent	ΔE_{rxn}[b]	k_{bim}[c]	efficiency, %	ΔE_o^*	ΔE_o^*	α
p-Me	−60.4	39.7	32.8	2.25	22.2	0.16
H	−58.9	23.1	18.5	2.85	22.8	0.18
m-F	−53.5	7.65	6.4	3.75	22.6	0.20
m-CN	−48.0	1.10	0.9	5.10	22.8	0.24

[a] As defined in Figure 1; units of kcal/mol. [b] Reference 12. [c] Units of 10^{-11} cm^3 molecule^{-1} s^{-1}.

constants k_{bim} obtained by monitoring benzyl anion depletion and bromide ion appearance were similar. The rate constants and efficiencies (efficiency = k_{bim}/k_{coll}, where k_{coll} is the ion–neutral collision rate constant[11]) are listed in Table I, along with overall energies of reaction[12,14] ΔE_{rxn}.

Experimental evidence[3] indicates that low-efficiency gas-phase nucleophilic processes occur along reaction coordinates with double minima. The rate of a reaction following such a potential surface is less than unit efficient due to the existence of the barrier between the wells. This situation has been shown to be amenable to an RRKM analysis.[3] By using frequencies and moments of inertia for the orbiting and S_N2 transition states as input parameters, and by matching experimental values of the branching fractions, one obtains the energy of the S_N2 transition state relative to that of the separated reactants[3] (Figure 1). Estimation of the $ArCH_2^-/CH_3Br$ well depths[15,16] as a constant 7.5 kcal/mol allows a determination of the activation energies ΔE^*. A plot of ΔE^* vs. ΔE_{rxn} (obtained by independent measurements[13]) gives a slope of 0.2. The slope is insensitive to the RRKM input parameters and independent of the well depth, provided the well depth is constant.

For the application of the Marcus equation, ΔE° for the "intrinsic" methyl transfer step must be estimated.[17] Since the overall exothermicity is so large, however, the expected small[18] variation in the $Br^-/ArCH_2CH_3$ well depths does little to affect the calculated value of the intrinsic barrier ΔE_o^*. More important are the choices for the RRKM input parameters. The parameters for the orbiting complex are well-defined;[19] therefore most of the uncertainty lies in the structure and vibrational frquencies of the S_N2 transition state, which give rise to different values of ΔE^*. Nonetheless, the values of ΔE^* are fairly insensitive to S_N2 transition-state entropy. Thus, the values of α are also insensitive to changes in S_N2 transition-state entropy, since they are calculated from the values of ΔE^* through eq 1. Varying the entropy as much as 25 eu (an enormous range for RRKM calculations[20]), by altering the frequencies of the three vibrations most sensitive to changes in structure and bonding, results in α varying only from 0.22 to 0.18. The values of ΔE^*, ΔE_o^*, and α are listed in Table I, taking $\Delta E^\circ = \Delta E_{rxn}$ and using S_N2 transition-state parameters about midway through the entropy range investigated. The plot of ΔE^* vs. ΔE° is linear, with a slope of ~0.2 as predicted from the Marcus intrinsic activation energy ΔE_o^* and the overall exothermicity, ΔE°.

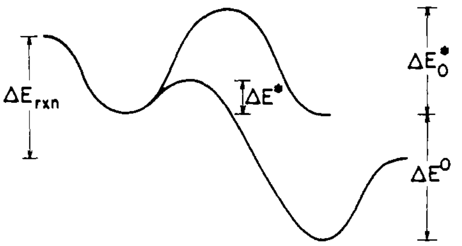

Figure 1. Relationship among the quantities ΔE^*, ΔE_o^*, and ΔE° in the Marcus equation, in the context of an exothermic gas-phase S_N2 reaction with a double-minimum potential.

In conclusion, we have demonstrated the consistency of the Marcus equation in application to S_N2 reactions by showing that the value of α predicted by the Marcus equation correctly predicts the slope of a Brønsted plot.[21] Our results thus strongly support the idea that the activation energy can indeed be considered as the sum of an intrinsic activation energy plus a term associated with the overall exothermicity of the reaction. Accordingly, our calculation[3] of these intrinsic barriers appears justified.

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Registry No. F^-, 16984-48-8; $ArCH_2^-$ (Ar = *p*-MeC_6H_4), 59305-42-9; $ArCH_2^-$ (Ar = Ph), 18860-15-6; $ArCH_2^-$ (Ar = *m*-FC_6H_4), 72611-56-4; $ArCH_2^-$ (Ar = *m*-NCC_6H_4), 72611-58-6; CH_3Br, 74-83-9; *m*-cyanotoluene, 620-22-4; *p*-methylbenzyltrimethylsilane, 7450-04-6; benzyltrimethylsilane, 770-09-2; *m*-fluorobenzyltrimethylsilane, 772-48-5.

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(10) Benzyl anions were generated by reaction of F^- with an appropriate precursor, either the toluene (*m*-CN) or benzyltrimethylsilane (*p*-Me, H, *m*-F). Corrections were made for ion loss and for reaction of F^- with CH_3Br.

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(12) ΔE_{rxn} for the unsubstituted benzyl anion was determined from Benson's values (Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976) and the known electron affinity of benzyl radical (Richardson, J. H.; Stephenson, L. M.; Brauman, J. I. *J. Chem. Phys.* **1975**, *63*, 74–76. Drzaic, P. S.; Brauman, J. I. *J. Phys. Chem.*, in press). For the substituted anions E_{rxn} was calculated from the known acidities of toluenes[13] and the assumption of constant C_α–H and C_α–C_β bond strengths in toluenes and ethyl benzenes, respectively.

(13) Taft, R. W., Mashima, M., personal communication.

(14) We assume that alkylation is occurring at the α-carbon. See: Russell, G. A. *J. Am. Chem. Soc.* **1959**, *81*, 2017–2022.

(15) (a) Dougherty, R. C.; Roberts, J. D. *Org. Mass Spectrom.* **1974**, *8*, 81–83. (b) Kebarle, P., personal communication.

(16) In the absence of strong hydrogen bonding the ion–neutral well depths are relatively independent of ion structure.[18]

(17) Potential energies have been substituted for free energies.[2,3b]

(18) French, M. A.; Ikuta, S.; Kebarle, P. *Can. J. Chem.* **1982**, *60*, 1907–1918.

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Useful Chiral Packing Materials for High-Performance Liquid Chromatographic Resolution of Enantiomers: Phenylcarbamates of Polysaccharides Coated on Silica Gel[1]

Yoshio Okamoto,* Mitsunobu Kawashima, and
Koichi Hatada

Department of Chemistry
Faculty of Engineering Science, Osaka University
Toyonaka, Osaka 560, Japan

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Resolution of enantiomers by liquid chromatography on chiral stationary phases has become a practically useful method for obtaining optical isomers and determining their purities.[2] Microcrystalline cellulose triacetate, which is prepared by heterogeneous acetylation,[3] is a useful stationary phase and has been widely employed for the resolution of aromatic compounds.[4]

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(1) Chromatographic Resolution 7. Part 6: ref 5.

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