2738 *J. Org. Chem.* **1997,** *62,* 2738−2741

α-Effect with Substituted *N*-Methylbenzohydroxamates and Substituted Phenyldimethylsulfonium Salts: Toward Understanding of an Intrinsic α-Effect

K. R. Fountain,* Timothy W. Dunkin, and Kamlesh D. Patel

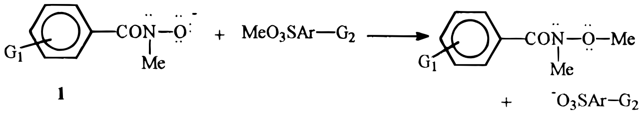
Truman State University, Kirksville, Missouri 63501

Received October 25, 1996[⊗]

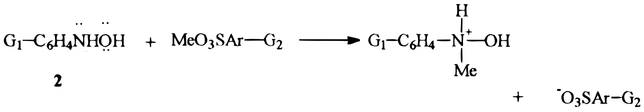
Increasing electron demand in the reactions of G-NMBH anions with substituted phenyldimethylsulfonium ions decreases the α-effect for the methyl transfers toward 1.0 (zero effect). An extrapolation shows the possibility of an inverse effect (<1.0). The reactivity of G-NMBH anions correlates with SET parameters and with the known propensity of phenyldimethylsulfonium ions to accept a single electron into a σ^* C−S orbital concomitant with expulsion of a CH_3 group. These correlations indicate inclusion of some SET character into the wavefunction of the S_N2 transition state for these reactions, in agreement with the Shaik and Pross SCD model of the S_N2 reaction.

Introduction

Recent studies of the α-effect, which is defined as enhanced reactivity on a Brönsted-type plot (log k_{nuc} vs pK_{anucH^+}),[1] in methyl group transfers have shown small α-effects (α-effect = $k_{\alpha-nuc}/k_{nuc}$, when the two nucleophiles have matching pK_a values). Buncel showed the effect with peroxide anions[2] (5.7−11.0) and hydrazine[3] (3.0−5.2) with phenylsulfate anion as the leaving group. Our group found α-effects of 2.48−3.5 with substituted *N*-methylbenzohydroxamate anions (G-NMBH) (**1**) vs substituted arenesulfonates, reaction 1, and with *N*-phenylhydroxylamines (NMPHA) (2.06−11.3) vs substituted arenesulfonates, reaction 2. (NOTE: The electrons shown on neighboring atoms in **1,** designated in this paper as G-NMBH or G_1-NMBH as the context demands it, are the distinguishing electronic structural feature of α-nucleophiles and are included for emphasis.)



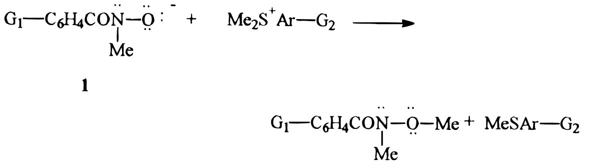
(1)



$$G_1{-}C_6H_4\ddot{N}H\ddot{O}H + MeO_3SAr{-}G_2 \longrightarrow G_1{-}C_6H_4{-}\overset{H}{\underset{Me}{\overset{+}{N}}}{-}OH + {}^-O_3SAr{-}G_2 \qquad (2)$$

2

In these two cases the point was made that the α-effect was expressed in S_N2 reactions with both charge dispersal ($\delta-$ on both the nucleophile and the leaving group) and creation of opposite charge ($\delta+$ on nucleophile and $\delta-$ on leaving group).[5] This paper reports the α-effect for S_N2 reactions with neutralization of charge. Reaction 3 shows the G-NMBH anions, **1**, reacting with substituted phenyldimethylsulfonium salts (fluoroborates), which are the methylating agents of this study.



$$G_1{-}C_6H_4CO\underset{Me}{\ddot{N}}{-}\ddot{O}:^- + Me_2S^+Ar{-}G_2 \longrightarrow G_1{-}C_6H_4CO\underset{Me}{\ddot{N}}{-}\ddot{O}{-}Me + MeSAr{-}G_2 \qquad (3)$$

1

The purpose of this report is to present the data from reaction 3, where the substrate aryldimethylsulfonium ions were believed to react by incorporating some single-electron acceptor character concomitantly expelling a $CH_3^{\bullet}$ radical.[25] If this single-electron transfer (SET) character is important in expressing the α-effect, then correlation of an α-effect with electron demand and typical SET experimental and theoretical results should be observed.

Experimental Section

The kinetics of reaction 3 were followed by our previously reported ^{1}HNMR kinetic method, modified by using 1,1,1-trichloroethane as an internal standard at 30 °C (±0.3).[4] Temperature control was provided by the Varian XL 200 NMR VT probe used in the earlier studies. The kinetic solutions were made up in pycnometers of 1.00 mL certified capacity in 0.05−0.02 M concentrations in methanol-d_4 and then mixed thoroughly before insertion into the probe. Plots of I_{std}/I_t gave straight lines ($r = 0.99$) (for the rate law rate = $k/(A - x)^2$ for second-order kinetics with equal concentrations for a minimum of 3−4 half-lives. In the cases of very fast reactions, i.e., with G_1 = 4-MeO, the reaction was followed to completion. The reaction mixture solutions were always very clean, showing only the products of reaction 3.

G_1-NMBH anions are reported in the previous study.[4] Substituted phenyldimethylsulfonium fluoroborates are all previously reported and had physical properties consistent with previous preparations.[6,7]

---

* Corresponding author: tel, (816) 785-4633; fax, (816) 785-04045; e-mail, sc18@truman.edu.

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

[1] (a) Edwards, J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 16. (b) Bunnett, J. F. *Annu. Rev. Phys. Chem.* **1963**, *14*, 271. (c) Fina, N. J.; Edwards, J. O. *Int. J. Chem. Kinet.* **1973**, *5*, 1. (d) Hoz, S.; Buncel, E. *Tetrahedron Lett.* **1984**, *25*, 3411.

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

[3] Buncel, E.; Chuaqui, C.; Wilson, H. *J. Org. Chem.* **1980**, *45*, 3621.

[4] Fountain, K. R.; Fountain, D. P.; Michaels, B.; Meyers, D. B.; Salmon, J. K.; Van Galen; D. A.; Yu, P. *Can. J. Chem.* **1991**, *69*, 798.

[5] Fountain, K. R.; Hutchinson, L. K.; Mulhearn; D. C.; Xu, Y.-B. *J. Org. Chem.* **1993**, *58*, 7883.

[6] (a) Lewis, E. S.; Hue, D. D. *J. Am. Chem. Soc.* **1984**, *106*, 3342. (b) Lewis, E. S.; Vanderpool, S. R. *J. Am. Chem. Soc.* **1977**, *99*, 1946. (c) **1978**, *100*, 6421. (d) Lewis, E. S.; Kukes, S.; Slater, C. D. *J. Am. Chem. Soc.* **1980**, *102*, 1619. (e) Lewis, E. S.; Smith, M. J.; Christie, J. J *J. Org. Chem.* **1993**, *58*, 7883.

[7] Fountain, K. R.; Patel, K. D.; Dunkin, T. W.; Powers, J. A.; Van Galen, D. A. *J. Org. Chem.* **1997**, *62*, 853−856.

S0022-3263(96)02002-6 CCC: $14.00

Table 1. Reactivity of G-NMBH Anions with Phenyldimethylsulfonium Ions at 30 °C in Methanol-d_4

nucleophile, G_1	substrate, G_2	$k \times 10^3$ (SD)	α-effect
4-MeO	H	210 (15)	8.45
4-NO_2	H	12.5 (0.3)	1.89
3,5-diNO_2	H	4.1 (0.01)	1.32
4-Cl	H	30.1 (2)	
H	H	100 (15)	2.24
H	4-NO_2	864 (45)	
H	4-CN	334 (20)	
H	4-MeO	51 (5)	

Results

Table 1 summarizes the kinetic data, and Figures 1 and 2 show Brönsted-type plots and a Brönsted-type–Lewis plot for the leaving group behavior, defined for phenyldimethylsulfonium fluoroborates (from the data of Lewis et al.[6]) as pK_{lg}^{Me}. The Brönsted-type plot for phenolate anions[8] vs substituted phenyldimethylsulfonium ions is reported in Figure 1 for comparison of the sizes of the α-effects.

Discussion

The α-effect expressed in Figure 1 indicates that, at least for this system, electronic effects are probably the major component. An argument could be made that the differences in the sizes of the α-effect are due to solvation varying with the electronic substituent effect. This variance would require those G-NMBH anions having electron-withdrawing substituents to be more tightly solvated in a hydrogen-bonding (deuterium-bonding) solvent, thus showing diminished reactivity relative to the comparison phenolate anion in order to show a diminished α-effect. The substituents on both kinds of nucleophiles are all very similar and should produce similar solvation effects at both nucleophilic sites. The only serious candidate for another explanation seems to be that the resonance interactions of the substituents with the sites of nucleophilic character differ. The possibility of through-resonance exists in phenols but not in the G-NMBH anions. This issue has been successfully dealt with in the first paper in this series;[4] in essence there is no effect on the nucleophilicity at the O-portion due to resonance in the phenolate series.

Hoz and Buncel[9] have critically examined the α-effect and its origin. The hypothesis of low basicity for the α-nucleophiles was discarded as a source of the reactivity enhancement. These workers also argued persuasively that ground state destabilization cannot be the cause of the α-effect.[10] Their argument is, briefly, that ground state destabilization requires that the magnitude of the α-effect goes to zero as β_{nuc} goes to 1.0. This is contrary to fact.

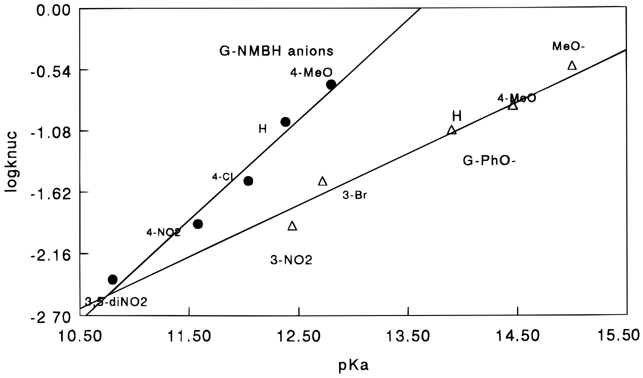


Figure 1. Brönsted-type plots of the reactivity of G-NMBH and G-PhO^- vs PhS^+Me_2 in methanol-d_4 at 30 °C.

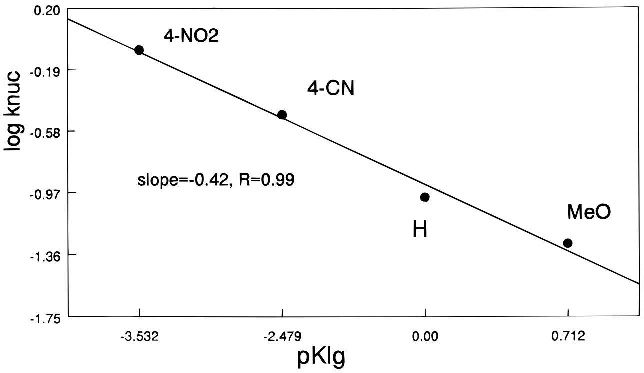


Figure 2. Brönsted-type–Lewis plot of the reactivity of NMBH vs G-$C_6H_4S^+Me_2$ in methanol-d_4 at 30 °C.

Solvents affect the size of the α-effect, as typified by studies of *p*-nitrophenylacetate with butane-2,3-dione monoximate anion[11] and α,α,α-trifluoroacetophenone oximate anion[12] in DMSO–water mixtures. The size of the α-effect changed in the two solvents and the mixtures, reaching a maximum at ca. 50 mol % DMSO, but complete elimination of the α-effect was not achieved. This behavior is expected from an electronic α-effect that was intrinsic but modified by a nonintrinsic entity such as solvent interactions. Indeed, Buncel and Um point to the need to dissect the α-effect into initial state and transition state contributors.[11]

Increasing electron demand[13] (or supply) in the G-NMBH anions diminishes (increases) the α-effect at substituted phenyldimethylsulfonium ions. Figure 1 indicates there exists a point at which electron demand is sufficient to give no α-effect, i.e., $k_{\alpha-nuc}/k_{nuc} = 1.0$; moreover, extrapolation shows the α-effect becomes inverse (<1.0) with still greater electron demand. The realization that the α-effect, at least for these G-NMBH anions, is an electronic one that is modified by solvent effects allows a discussion of an intrinsic α-effect, which is modified by other factors in each reaction circumstance. A preliminary discussion to this end has been advanced[4] and can now be extended.

Table 2 summarizes the data for discussion. The change in charge type from dispersal of negative charge (with O_3SAr anions as leaving groups) to cancellation of charge (with MeSAr as leaving group) produces little change in the size of the α-effect, except that expected from increasing electron demand. The similarity in the β_{nuc} values of the G-NMBH anions for the two different charge types indicates (perhaps coincidentally) very similar nucleophilic behavior. The β_{lg}^{Me} parameter shows a large difference in the departure of the two leaving groups (0.44 vs 0.42), and the corresponding apparent bond orders (BO) ($1.0-\beta_{lg}^{Me}$ for the BO to the leaving

---

[8] Fountain, K. R.; Patel, K. D.; Duncan, T. W. The Reactivity of Substituted Phenyldimethylsulfonium Ions with Common Nucleophiles. A Test of PK_{lg}^{Me} for Phenyldimethylsulfonium Ions and a Comparison with methylarenesulfonates. Manuscript in revison.

[9] Hoz, S.; Buncel, E. *Isr. J. Chem.* **1984**, *26*, 313.

[10] Buncel, E.; Hoz, S. *Tetrahedron Lett.* **1983**, *24*, 4777.

[11] Buncel, E.; Um, I.-H. *J. Chem. Soc. Chem. Commun.* **1986**, 595.

[12] Laloi-Diard, M.; Verchere, J. F.; Gosselin, P.; Terrier, F. *Tetrahedron Lett.* **1984**, *25*, 1267.

[13] Isaacs, N. S. *Physical Organic Chemistry*; Longmans Scientific and Technical: New York, 1987; pp 129–132.

Table 2. Summary of α-Effect Data for G-NMBH Anions

electrophile	β_{nuc}	$\beta_{\mathrm{lg}}^{\mathrm{Me}}$	α-effect	charge type	solvent	ref
p-nitrophenylacetate	0.23		45	$\delta-,\delta-$	12% EtOH/H_2O	14
benzyl bromide	0.31		13	$\delta-,\delta-$	12% EtOH/H_2O	15
methyl arenesulfonates	0.86	0.44	2.5−3.5	$\delta-,\delta-$	methanol-d_4	4
	0.80		3.5−4.8	$\delta-,\delta-$	H_2O−20% dioxane	4
phenyldimethylsulfonium	0.85	0.42	0.6−8.45	$\delta-,\delta+$	methanol-d_4	this work

Table 3. Summary of Bond Order Information from Brönsted Type and Brönsted Type−Lewis Plots for Nucleophilic Attack on Methyl Arenesulfonates and Phenyldimethylsulfonium Ions

	BO		
system	nuc (β_{nuc})	leaving grp ($1.0-\beta_{\mathrm{lg}}^{\mathrm{Me}}$)	ΣBO
G-NMBH-MeO_3SAR	0.86	0.56	1.42
G-NMBH-Me_2S^+Ar	0.85	0.58	1.43
G-PhO^- MeO_3SAR	0.31[a]	0.54	0.85
G-PhO-Me_2S^+Ar	0.45	0.46	0.91

[a] Computed analytically from data obtained by competition experiments

group) are 0.56 and 0.58 between the C atom and the methyl aryl sulfide leaving groups. Some comment on the meaning of this difference in the size of $\beta_{\mathrm{lg}}^{\mathrm{Me}}$ is in order. Small differences in this parameter are accepted in the literature as meaningful.[27] With methyl arenesulfonates a difference of 0.45−0.47 indicated a change from neutral ethanol to ethoxide.[27a] The S_N2 displacement of allyl from arenesulfonates had a $\beta_{\mathrm{lg}}^{\mathrm{Me}} = 0.51$, indicating π assistance, *exo*-norbornyl arenesulfonates had $\beta_{\mathrm{lg}}^{\mathrm{Me}} = 0.57$, and cyclobutyl had 0.55. In each case the larger $\beta_{\mathrm{lg}}^{\mathrm{Me}}$ was associated with a greater electronic assistance in promotion of bond cleavage between C and the O_3SAr group. The regression coefficients for these literature determinations ranged from 0.992 to 0.998. Figure 1 shows very comparable *R* values for the present work, and the difference ($0.44-0.42 = 0.02$) is consistent with the interpreted literature differences. These facts indicate that interpretation of our differences in $\beta_{\mathrm{lg}}^{\mathrm{Me}}$ is warranted. Apparently the smaller $\beta_{\mathrm{lg}}^{\mathrm{Me}}$ is associated with the better nucleophile toward aryldimethylsulfonium ions in the present case. Apparently the methyl aryl sulfide responds more to the transfer of large amounts of charge than the arenesulfonates. The exact nature of the response of methyl arenesulfonates to nucleophiles is yet nearly unexplored.[8] The difference between the β_{nuc} value for the phenolates (0.45)[8] and the G-NMBH anions (0.85) and the $\beta_{\mathrm{lg}}^{\mathrm{Me}}$ values for these two anionic systems indicates something fundamentally different occurs in their respective transition states.

Table 3 shows the sums of the bond orders to C at the transition state for the two nucleophilic−electrophilic systems. A trend is clear that the G-NMBH anions contribute more charge to the S_N2 transition state (TS) than the phenolate "normal nucleophiles".

The major question implicit in Table 3 is "Where does the extra charge in the TS go?" At least a partial answer comes from the study of AIM[17]-based bond lengths and charge distributions in methanol and methoxide by Wiberg.[16] In this study the excess charge distribution on the O^- atom in methoxide is spread into the H atoms, giving a shorter C−O bond than in methanol. Similarly, Shi and Boyd, using the Bader population analysis at high levels of theory (MP2//6-31++G**),[18] point to negative charge deposited on H atoms in S_N2 transition states.

A similar occurrence is possibly the case with the present systems. Accepting the putative sum of bond orders to C in Table 3 for normal nucleophiles as ca. 0.88 (averaged), then for the G-NMBH-Me_2S^+Ar system an excess of 0.14 electron/H atom would have to be accommodated over the amount in a normal nucleophilic attack. The necessity for H atoms to bear all this excess charge is lessened by the ability of the leaving group to withdraw charge in the transition state. The phenyl sulfates, arenesulfonates, and methyl sulfides are apparently quite good at this charge withdrawal; thus they show the α-effect. With a less good leaving group no α-effect, or a much diminished one, would occur. Reports of no α-effect with halide leaving groups[19] are consistent with less ability to take away negative charge from the C atom in the TS. These ideas are consistent with Bordwell's discussion of factors previously recognized as favoring electron transfer from a nucleophile to an electrophile, RX.[20] A strong electron receptor in R is one such prominent factor.[21]

Other lower LUMO (LL) substrates,[22] such as >C=O groups, exhibit greater α-effects because they disperse the negative charge from the C atom to the O atom, where it is more accessible to H-bonding in donor solvents.[4] This idea of an intrinsic electronic α-effect which is modified by extrinsic factors, such as transfer of excess charge to atoms where H-bonding can stabilize it, can be substantiated within the current models of nucleophilic behavior. The next sections discuss this.

Shaik's SCD model for the S_N2 transition state[26] combined with Hoz's model for the α-effect[22] afford reasonable models to accommodate our data. These models are particularly compelling because of the known ability of aryldimethylsulfonium ions to undergo SET concomitantly with expulsion of a group, such as $CH_3^{\bullet}$. Saeva et al.[23] have specifically examined this point and report that, in contrast to preliminary capture of an electron to give a sulfuranyl or aryl radical anion,[24] electrochemical data are consistent with a concerted σ S−C bond breaking concomitant with electron acceptance. This conclusion was subsequently modified by Savèant, Saeva, et al.[25] who show in electrochemical experiments that capture of an electron in SET transac-

---

(14) (a) Dessolin, M.; Laloi-Diard, M.; Vilkes, M. *Tetrahedron Lett.* **1975**, 2405. (b) Dessolin, M.; Laloi-Diard, M. *Bull. Soc. Chim. Fr.* **1971**, 2946.

(15) (a) Aubort, J. D.; Hudson, R. F. *Chem. Commun.* **1970**, 937; (b) 938; (c) 1378.

(16) Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 3379.

(17) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *9*, 18 references therein.

(18) Shi, Z.; Boyd, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 1575.

(19) Gregory, M. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1967**, *89*, 4400.

(20) Bordwell, F. G.; Clemmens, A. H. *J. Org. Chem.* **1981**, *46*, 1036.

(21) Kornblum, N. *Angew. Chem., Int. Engl. Ed.* **1975**, *14*, 734.

(22) Hoz, S. *J. Org. Chem.* **1982**, *47*, 3545.

(23) Saeva, F. D.; Morgan, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4121.

(24) Beak, P.; Sullivan, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 4450.

(25) (a) Andrieux, C. P.; Robert, M.; Saeva; F. D.; Savèant, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 7864. (b) Saeva, F. D.; Breslin, D. T.; Martic, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 1328.

(26) Shaik, S. S.; Schlegel; H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry*; John Wiley & Sons, Inc.: New York, 1992; Chapter 4.

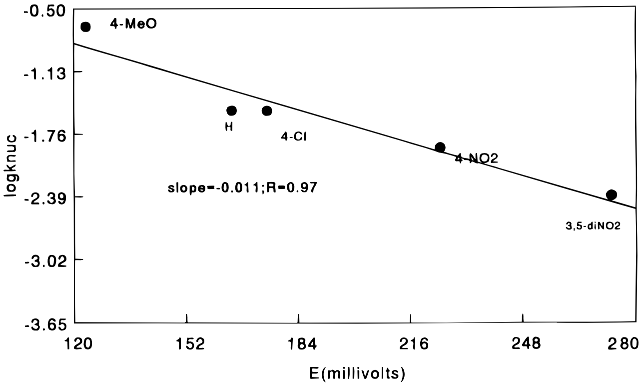


Figure 3. Correlation of the oxidation potentials ($E_{1/2}$) of G-NMBH vs reactivity with PhS^+Me_2 in methanol-d_4 at 30 °C.

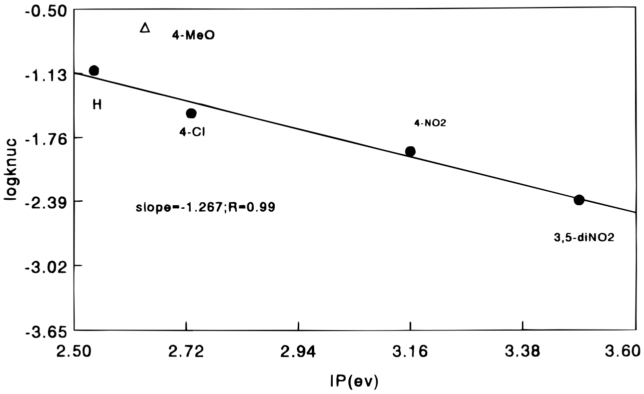


Figure 4. Correlation of the Koopmans' theorem ionization potentials of G-NMBH vs reactivity with PhS^+Me_2 in methanol-d_4 at 30 °C.

tions with these substrates is nearly concomitant with loss of $CH_3^\bullet$. The electron is inserted into a σ^* C−S orbital and not into a π^* orbital.[26b] In the electrochemical study the phenyldimethylsulfonium ions, though proceeding through an "EC" mechanism, were shown to have the electron transfer step participating more significantly in the mixed kinetic control than with the naphthyl or 9-anthracenyl systems. Factors they cited that contribute to a more concerted process were (1) high orbital energies and (2) weak bonds. In the present case the source of electrons, the nucleophile, also captures the CH_3 group, thus making the expulsion of this group from the S atom a much lower energy process. Something similar occurs with phenyldialkylsulfonium ions that have more stable groups (benzyl) than CH_3 groups. The electron capture in an electrochemical experiment for these groups is then completely concerted with group expulsion. This leads to the plausible conclusion that in the present case any SET character transferred in the transition state would be concerted with group expulsion (capture by the nucleophile). Such SET character ought to be manifested by the correlation with such typical SET parameters as the ionization potentials and oxidation potentials of the nucleophiles.

The SCD model requires the inclusion of some SET character into the S_N2 transition state, as shown by the correlation of the excited state ($Y^\bullet[R^\bullet:X]^-$) of the collision complex, ($Y:^-[R:X]$)CH. Note that this model requires SET character from both the nucleophilic side and the leaving group side. The Hoz model for the α-effect mixes the SET character into the total TS wavefunction by the four-electron-splitting diagram, where the increased stability is retained upon transfer of a single electron.[22]

Figures 3 and 4 show plots of the reactivity of the G-NMBH anions in (3) vs ionization potential (IP, Koopmans' theorem from AM1) and vs $E_{1/2}$(ox). The correlations are quite good except that the 4-MeO point plots above the line in Figure 4. This point also plotted off the line in a similar plot for methyl arenesulfonates, reaction 1. Figure 4 neglects this point in the regression. These figures make the point that the G-NMNBH anions' reactivity correlates well with typical single-electron parameters. The combination of the correlations of these reactivities with SET behavior and the reported concomitant acceptance of a single electron and the expulsion of a methyl group[23,26] make a compelling case that the α-effect, at least in this system, has a considerable SET character mixed into the wavefunction of the transition state.

Conclusions

The decrease in the α-effect with increasing electron demand in the G-NMBH anions is probably best ascribed to an electronic effect with phenyldimethylsulfonium ions. Correlation of the reactivity of G-NMBH anions with SET parameters indicates inclusion of some SET character in the transition state. This agrees with the known propensity of substituted phenyldimethylsulfonium ions to accept an electron into a σ^* C−S orbital with concomitant expulsion of a $CH_3^\bullet$ group. The reception of this group by the nucleophile lowers the energy necessary for the C−S bond cleavage, thus making the SET character and CH_3 group expulsion more concerted than in the electrochemical experiments.

Acknowledgment. We gratefully acknowledge support of this work from the National Science Foundation in RUI Grant CHE-962663. We also thank the referees for patience and insightful comments.

JO9620021

---

(27) (a) Hoffman, R. V.; Shankweiler, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 5536. (b) McManus, S. P.; Smith, M. R., Jr.; Shankweiler, M.; Hoffman, R. V. *J. Org. Chem*, **1988**, *53*, 141 and references therein.