The α-Effect in Benzyl Transfers from Benzylphenylmethyl Sulfonium Salts to *N*-Methylbenzohydroxamate Anions

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The investigation of the occurrence of the α-effect in group transfers from phenyldialkyl sulfonium ions where one alkyl group is benzyl allows an assay of the effect of changing the nature of the C atom being transferred. The size of the α-effect responds to increasing electron demand, as methyl transfers do. Quantitative relationships between the size of the α-effect are established from both the nucleophilic side and the leaving group side of the S_N2 transition state.

Introduction

The α-effect is the term used to describe the enhanced nucleophilic activity of nucleophiles with the structure **1**. It is shown on a Brönsted-type plot of the α-nucleophile and a normal nucleophile (without the extra lone pair) over a convenient range of pK_a values for both nucleophiles. Two equivalent ways of expressing the effect are known because Brönsted-type plots correlate log k_{nuc} with pK_a[1] of the conjugate acid of the nucleophile. Both the ratio of rate constants, $k_{α-nuc}/k_{nuc}$, and log $k_α$ − log k_{nuc} at a particular pK_a value on the Brönsted-type plots are used for quantitative expressions of the α-effect ($k_α$ is a the rate constant for the α-nucleophile.) We use both expressions in this paper.

$$\overset{..\quad..}{X-N}$$

1

A Stylized α-Nucleophile

Recent reports[2−4] show that *N*-methylbenzohydroxamate (NMBH) anions display an α-effect of ca. 2−10 (rate constant ratios) in methyl transfers from arylsulfonate ions and arylmethyl thioethers, [1]. Methyl transfers from aryldimethyl sulfonium salts to NMBH anions show a decrease in the size of the α-effect (Δ log *k*) on a Brönsted-type plot of the log *k* vs pK_a values for both the simple nucleophile and the α-nucleophile[4] as the electron demand on the NMBH is increased. Reaction [2] demonstrates that the variation in the Ar portion of the leaving group correlates with increasing ability to receive SET character in electrochemical experiments,[4] because the size of the α-effect follows phenyl < 1-naphthyl < 9-anthracenyl—the same order as for acceptance of SET in electrochemical experiments.

The sensitivity (slope = $β$) of the α-nucleophiles plot is greater than for the normal ones, in [3], so the size of the α-effect (expressed as Δ log k_{nuc}) is smaller with increasing electron demand.

The α-effect must thus be at least partly electronic[3] in nature even when transferring CH_3 groups from these sulfonium ions. These plots indicate that some intrinsic part of the α-effect is due at least partially to electrical effects, even in methyl transfers, and these effects are important in teasing out the details of the α-effect.

Several authors have questioned the existence of the α-effect with methyl transfers.[9] The data showing that methyl group transfers between NMBH anions and arylmethyl thioethers respond to increasing electron demand allows the claim that the α-effect is at least partly electronic, at least in this system, with such items as solvent effects, or changes at the transferred C atom, such as making it a C=O or a −CH_3Ar group, modifying the size of the α-effect. The present paper reports on experiments performed to examine the behavior of the α-effect with structure changes on the C atom being transferred.

The current hypothesis is that such methyl group transfers to α-nucleophiles involve an intrinsic α-effect and that the modification of the type of C atom being transferred will modify the size of the α-effect. This idea is pursued in this paper using benzyl group transfer to examine how the reactivity parameters $β_{nuc}$ and $β_{lg}^{Me}$, LUMO−HOMO interactions, and electrochemically obtained single electron parameters from ref 5 correlate with these group transfers. Only the unsubstituted benzyl group is studied in this paper to avoid dealing with possible U-shaped curves, as suggested by Kim, Lee, et al.[7] with benzyl group transfers to phenoxides and thiophenoxides. Expectations include larger α-effects in
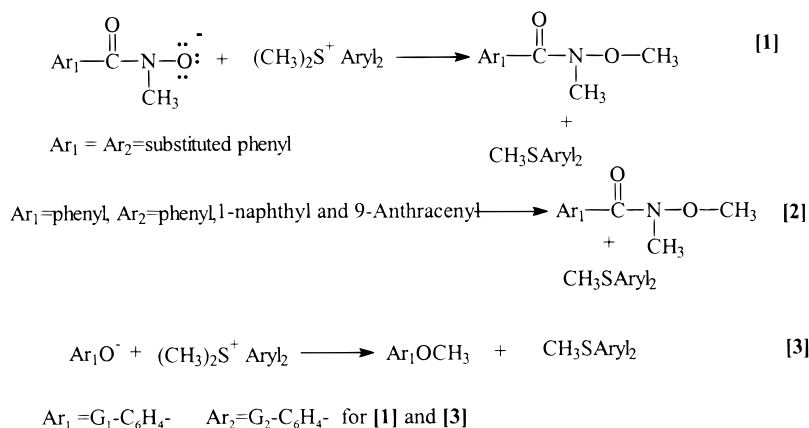
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$$Ar_1-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{N}-\overset{..}{\underset{..}{O}}:^- \quad + \quad (CH_3)_2S^+ Aryl_2 \longrightarrow Ar_1-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{N}-O-CH_3 \qquad [1]$$

$$+$$
$$CH_3SAryl_2$$

Ar$_1$ = Ar$_2$=substituted phenyl

$$Ar_1=phenyl, Ar_2=phenyl, 1\text{-naphthyl and 9-Anthracenyl} \longrightarrow Ar_1-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{N}-O-CH_3 \qquad [2]$$
$$+$$
$$CH_3SAryl_2$$

$$Ar_1O^- \quad + \quad (CH_3)_2S^+ Aryl_2 \longrightarrow Ar_1OCH_3 \quad + \quad CH_3SAryl_2 \qquad [3]$$

Ar$_1$ = G$_1$-C$_6$H$_4$-   Ar$_2$=G$_2$-C$_6$H$_4$- for [1] and [3]

benzyl transfer than in methyl, because the benzyl group, combined with the known ability of these aryl dialkyl sulfonium salts to receive single electron character,[5] should more greatly stabilize any radical character in the transition state. We can then expect more SET character in the transition state wave function. An excellent general consideration is reported by Shaik et al.[8b] In their treatment, the state correlation diagram (SCD) shown in Figure 5 and the VB contributors **A**−**D** supply a schematic view of the wave functions involved and their combinations to give the transition state (TS). Similar accounts appear in other sources.[6,15]

A test of this hypothesis comes from using a series of structural modifications of the transferred C atoms in a series of benzylphenylmethyl sulfonium salts. These salts characteristically undergo EC reactions (Scheme 1) with

Scheme 1
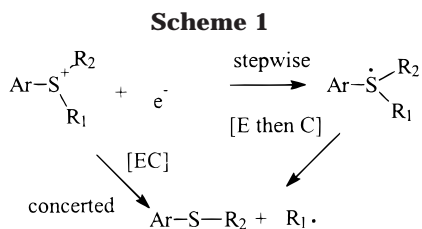
single-electron capture (E) and chemistry (C).[5] We have previously discussed methyl transfers in the series shown in [1] and [2]. Series [1] provided Brönsted-type plots (log k_{nuc} vs pK_a) that indicated decreasing sizes of α-effects with increasing electron demand in the NMBH anions compared with the reactivity of phenolate anions (normal nucleophiles). The demands of the SCD model indicate that structural modification on the C atom, making it into a benzyl C atom in the present case, ought to give greater reactivity in benzyl transfer. This greater reactiv-

ity is most easily seen in changes in their reactivity behavior.

This idea parallels the known tendency of the series of aryl dialkyl sulfonium salts in Scheme 2 to become
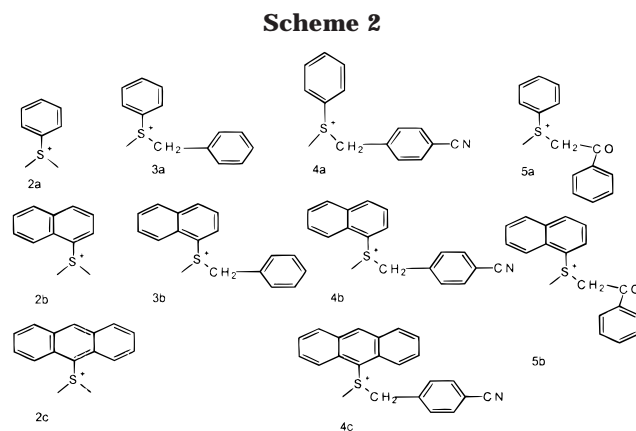
Scheme 2

more EC (concerted) as the bond between the S and the R group weakens.[5] The trend toward greater EC character increases toward benzyl and phenacyl groups in Scheme 2. We are thus testing the ability of a known concerted reaction involving benzyl transfers, in substrates of known single electron acceptor capacity, to express the α-effect.

Experimental Section

Materials. Benzylphenylmethyl sulfonium fluoroborates were produced by modifying the previously used procedure for the phenyldimethyl sulfonium ions.[3,4] The substituted aryl benzyl sulfides were made by reactions between the various substituted phenyl thiolates, made by reactions of NaOCH$_3$ with the substituted thiophenols (Aldrich, 99+%) and benzyl chloride in THF. After characterization by IR and ¹HNMR, the reaction with trimethyloxonium fluoroborate in dichloromethane gave the benzylphenylmethyl sulfonium fluoroborate.

Sodium salts of *N*-methylbenzohydroxamic acids (NMBH) were made as previously reported,[2] and their pK_a values in MeOH are available from prior studies.[2,4] Phenolate salts were made for reactions of NaOCH$_3$ in methanol with the respective phenols and NaOMe.

Kinetics

Kinetics for [2] were obtained analogously to our previous method for methyl transfers.[2,3] Table 1 shows the results as rate constants.

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Table 1. Rates of Reaction 4 in Methanol-d_4 (CD_3O^-) at 30.5 °C vs Ar_2=$C_6H_5^-$

XNMBH	k(L/mol/s) (SD)	k_{rel}[a]	pK_a
4-Me	1.8 (0.22)	257	12.45
H	0.43 (0.014)	43.2	12.38
4-Cl	0.393 (0.0034)	28	12.04
4-CF$_3$	0.24 (0.011)		11.77
4-NO$_2$	0.048 (0.000)	6.6	11.58
3,5-diNO$_2$	0.011 (0.0011)	1.0	10.8
	Phenolates		
4-Me	0.800 (0.036)	14.8	
H	0.245 (0.013)	14.46	
4-Br	0.060 (0.017)	13.61	
3,4-diCl	0.013	(0.006)	12.9
4-NO$_2$	0.0050(0.000)	11.5	

[a] By competition reactions.

Competition Experiments. A typical experiment follows:

A 1.0 mmol amount of each of the two substituted NMBH anions in the competition was dissolved in methanol-d_4 or methanol. To these solutions was added 0.1 mmol of benzylphenylmethyl sulfonium fluoroborate. The reactions were kept at a constant temperature of 30 °C (±0.5). After several hours, aliquots were removed for GCMS analysis of the benzylated NMBH products. Authentic material from reactions of the NMBH sodium salts with benzyl bromide gave both retention times and authentic MS to guide the experiment. The areas were digitally integrated. Since the GCMS instrument response has previously been found to be linear in grams,[2,4] we then computed the relative rates by converting the peak areas to moles, as previously reported.[2]

Leaving Group Behavior. The relative rates for reactions between benzyl-substituted phenylmethyl sulfonium salts and phenolate were obtained in competition experiments analogous to those of the substituted NMBH anions. Leaving group behavior of the phenolates was determined by reactions of 4-MeOC$_6$H$_4$O Na$^+$ and 3-NO$_2$C$_6$H$_5$ O$^-$ Na$^+$ with substituted phenylbenzylmethyl sulfonium fluoroborates in methanol-d_4 and methanol. Analysis of GCMS results for the ratios of substituted phenylmethyl thioethers, produced by reacting the substituted sulfonium salts with 4-MeOC$_6$H$_4$O$^-$, corrected for other reactions by running blank samples of just the sulfonium salts, and analysis for the other sources of the methylthioaryl ethers, gave the ratios of grams of thioethers responsible for the benzylation of the phenolate. The 3-NO$_2$C$_6$H$_4$O$^-$ relative rates we obtained by competition reactions between 4-Cl-NMBH anions and the 3-nitrophenolate, in 10-fold millimolar excess for a 1.0 mmol mole amount of substituted phenylbenzylmethyl sulfonium salt in MeOH in vials thermostated to 30(±0.5) °C These area ratios were corrected by conversion to moles as previously reported for this GCMS instrument.[2] The relative rate data were converted to absolute values from the previously determined absolute rate of 4-Me-C$_6$H$_4$O$^-$ with phenylbenzylmethyl sulfonium ions, and the reaction rates of the 4-ClNMBH anion in Figure 1. Some interpolation, using the regression equation of the ClNMBH in Figure 1, was necessary to determine the rates of the phenolates as ratios of the ClNMBH anions.

Computational Methods

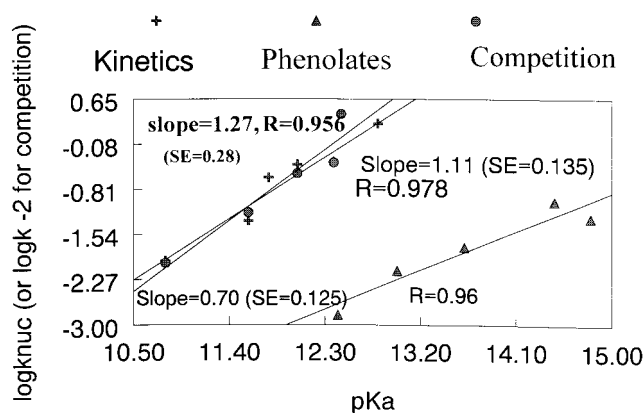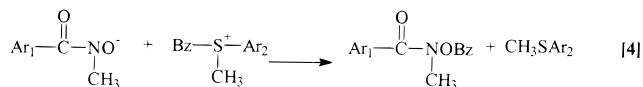All structures were completely optimized, using the PM3 UHF Hamiltonian in Hyperchem and showed only

Figure 1. Kinetics of the reactions of NMBH anions and phenolate anions with substituted phenyl benzylmethyl sulfonium ions in methanol-d_4 at 30 °C.

positive eigenvalues from diagonalization of the force constant matrix. The LUMOs for benzyl-substituted phenylmethyl sulfonium cations were computed.

Results

Kinetics. The kinetics were complex for [4]. Second-order plots showed considerable curvature after 30% reaction. Attempts to correct for first-order solvolysis by plotting dx/dt/[A−x] = k_2[A−x] + k_1 gave curved plots also, indicating another second-order process was occurring. We ascribed this second process to be S$_N$2 displacement at benzyl by CD$_3$O$^-$.

$$Ar_1-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{N}O^- \quad + \quad Bz-\overset{+}{\underset{\underset{CH_3}{|}}{S}}-Ar_2 \quad \longrightarrow \quad Ar_1-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{N}OBz \quad + \quad CH_3SAr_2 \qquad [4]$$

A first estimate of the rate constants by using only the first, linear 30% of the reaction, as suggested by Bunnett,[10] gave the rate constants in Table 1. Plotting the log k_{nuc} values vs the pK_a values of the NMBH acids gave the topmost line (boldface type) in Figure 1.

Plotting the log k_{rel} −2.00 vs the pK_a values for the NMBH competition reactions (see the Experimental Section) placed their line on the same scale as for the kinetic results with NMBH anions. The middle line (shaded circle) in Figure 1 for these kinetic data shows the two slopes of the lines for the NMBH anions are similar in magnitude. The slope was 1.27 for the competition experiments, so the previous kinetic results were valid despite using only the first 30% of each reaction. Table 1 summarizes the relative rate data.

Similarly, [4] was studied substituting variously substituted phenolates for the NMBH anions. Table 1 summarizes these rate constants also. Plotting the log k_{nuc} value for these phenolates vs pK_a gave the bottom line in Figure 1.

An important part of explaining the results from benzyl transfers refers to the habit of making the solutions basic by adding NaOMe-d_3 to the methanol-d_4 solutions. This is necessary to preserve the complete ionization of the NMBH anions.[2] In methyl transfers, no evidence of displacement at CH$_3$ by the strong base, MeO$^-$, was found in the presence of NMBH anions. However, some benzyl transfer to give the BzOCH$_3$ (D$_3$) compounds was ob-

Table 2. Rates of Substituted Benzylphenylmethyl Sulfonium Fluoroborates with 4-ClNMBH Anion and Phenolates at 30 °C in Methanol-d_4

	4-ClNMBH Anion	
G_2	k (L/mol/s)	p$K_{lg}^{Me\ 11}$
H	0.39	0.0
4-Cl	0.584	−0.744
4-Me	0.16	0.579
4-NO$_2$	12.8	−3.532
4-MeO	0.14	0.712
3-Cl [c]	0.83	−0.900

	Phenolates			
	4-MeOC$_6$H$_4$O$^-$		3-NO$_2$C$_6$H$_4$O$^-$ [b]	
		k_{abs} (L/mol/s)		k_{abs} (L/mol/s)
G_2	k_{rel} a	$\times 10^3$	k_{rel}	$\times 10^3$
H	0.576	430	1.89	210
4-Cl	0.635	473		239
4-Me	0.386	288		191
4-NO$_2$	1.000	745	16.9	370
3-Cl			2.90	238
4-MeO				222 [d]

[a] Measured by determination of relative amounts of Ar^{2}SMe produced. [b] Measured by competition reactions and then converted to absolute k values by multiplying by the rate constants from Figure 2 or interpolations, using 4-ClNMBH anion vs the leaving groups. [c] Interpolated from eq 7 and from ref 3 data and regression equations.

served in GCMS of the reaction mixtures. No evidence of methyl transfer was ever observed in any of the reactions of benzyl transfer. This result is consistent with the finding in Scheme 2 that no production of CH$_3$ radicals occurs when the production of benzyl radicals is possible[5] in the electrochemistry. The slope of the Brönsted-type plot for the NMBH anions was 1.11(±0.135), corresponding to a $\beta^\alpha_{nuc} > 1.0$. Because the explanation of such a parameter greater than 1.0 requires special considerations, we decided to check the validity of these rate constants by direct competition reactions. The log k_{rel}^α −2.00 for the substituted NMBH anions in competition experiments in Table 1 is plotted as the line indicated in Figure 1, indicated by a shaded circle. The slope of 1.27(±0.28) was within the allowed variance of the directly determined kinetics for the NMBH anions, thus validating our treatment by giving results consistent with the direct kinetic treatment.

Kinetics for [4] where Ar$_1$ is 4-ClC$_6$H$_4$ and Ar$_2$ is varied allowed determination of leaving group behavior in terms of pK_{lg}^{Me} values for methylphenylsulfides[11]. Table 2 summarizes the rate constant data. Plotting the log k vs pK^{Me}_{lg} for this reaction gave the top line in Figure 2. The slope (β_{lg}^{Me}) was 0.39. Table 2 also shows the results for two phenolates, which give the bottom line in Figure 2. The β_{lg}^{Me} was 0.09 (±0.02) when the log k values of the nucleophiles was plotted vs −pK_{lg}^{Me} for the 4-MeOC$_6$H$_4$O$^-$ and was 0.061(±0.03) for the 3-NO$_2$C$_6$H$_4$O$^-$.

Table 3 summarizes the reactivity β parameters for [1] and [4]. The parameters, β^α/β_{nuc}, give the ratios of susceptibility of the two kinds of nucleophiles to substituent effects, and the slope of an ELUMO (energy of lowest occupied molecular orbital) of the sulfonium salts vs log k plots shows the sensitivity of [4] to the ease of placing a single electron into the electrophile. The range of the α-effect is $\Delta\delta$ log k, using the β log k values between the α-nucleophile and a pK_a-matched phenolate anion
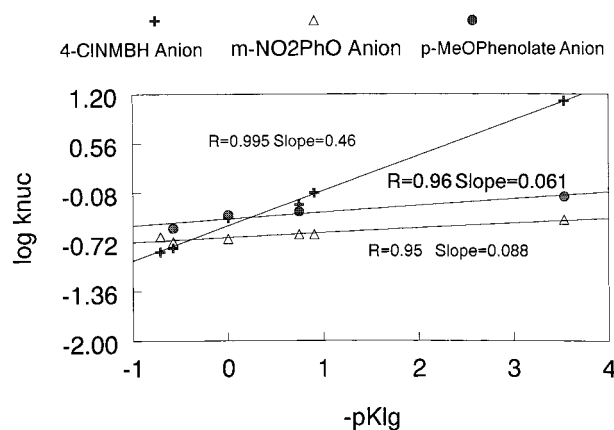
Figure 2. Leaving group behavior of reaction 4 in methanol-d_4 at 30 °C. Nucleophiles vs substituted sulfonium salts.

Table 3. Comparison of Group Transfer Parameters for Reactions 1 and 4

group transferred	β^α/β_{nuc}	range of α-effect (log units)	slope of ELUMO plot vs logk_{nuc}
Me	0.84/0.45 = 1.88	0.93−0.12	1.06
Bz	1.11/0.66 = 1.68	2.36−1.1	2.03
Bz from BzBr [a]	0.30/0.29 = 1.03[13]	1.176−1.00[12]	NA

[a] 50% aqueous acetone at 25 °C.
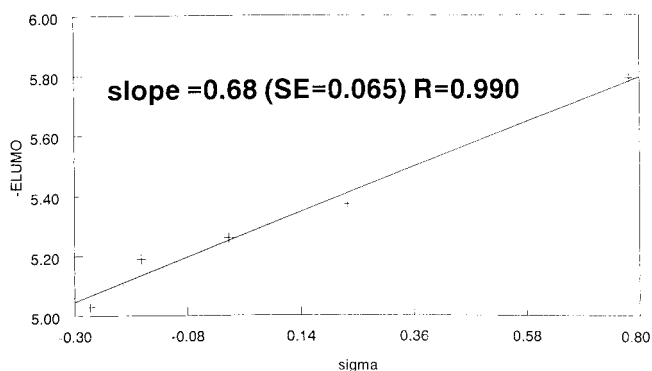
Figure 3. Hammett plot for correlation of ELUMO with rate constants of reaction 4.

from Figure 1, and the analogous effects from the plots for methyl transfers.[3] The largest α-effect computed by this method was limited only to experimental data for the most reactive nucleophile, but the corresponding phenolate data were computed from the correlation line for phenolate, when this was needed (i.e., when no phenol closely matched the observed α-nucleophile pK_a).

The plot of log k_{nuc} vs the ELUMO (not shown) shows the greater dependence of benzyl transfers on the ability of the benzylmethylarylsulfonium salts to receive SET character compared to methyl transfer from dimethylarylsulfonium salts.

Correlations of Data with LUMO Energies. A plot of the LUMO energies of the sulfonium (ELUMO) salts vs Hammett parameters gave the results in Figure 3, showing that correlation of these ELUMOs was possible. When the δ log k (= α-effect) from k_{nuc} values of the benzylmethylarylsulfonium salts with 4-ClNMBH and 3-NO$_2$C$_6$H$_4$O$^-$ were plotted Figure 4 resulted, giving the behavior of the fraction of the α-effect for the leaving
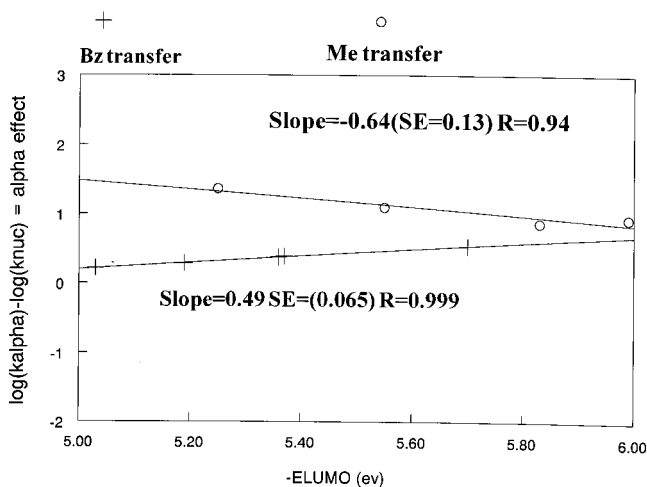
Figure 4. Correlation of leaving group behavior with ELU-MO.

Table 4. ELUMO Values of Substituted Phenylbenzylmethyl Sulfonium Ions

substituent	ELUMO (eV)	substituent	ELUMO (eV)
H	−5.36	4-MeO	−5.03
4-Cl	−5.37	4-NO$_2$	−5.79
4-Me	−5.19		

group as a function of ELUMO for both methyl and benzyl transfer. The ELUMO data for the methyl transfers are from ref 11. The α-effect data for both 3-nitrophenolate and NMBH for the leaving groups in methyl transfers are from refs 3 and 19. A sample calculation of the α-effect for the leaving groups in methyl transfers is given below. From Figure 2 in ref 19 the log k_{nuc} value is −2.097. (The k_{nuc} values in Table 1 of ref 3 for the 3-NO$_2$C$_6$H$_4$O$^-$ nucleophile are all actually 10 times bigger. The plot in Figure 2 is correct.) The NMBH anion data are from Table 1 of ref 19 for the unsubstituted phenyldimethyl sulfonium salt. Log k_{nuc}^{α} = −1.00. The difference in log terms = α-effect = −1.097. This value is plotted vs the −ELUMO (5.55 eV) for phenyldimethyl sulfonium ion in Figure 4. Similarly, all the data from the different published papers are represented in Figure 4.

Table 4 shows the ELUMO data for correlations of the size of the α-effect vs ELUMO of the electrophiles.

Discussion

To summarize the behavior of the size of the α-effect from both the nucleophile side and the leaving group side of the transition state (TS) it is useful to derive the α-effect from the regression equations of the plots. This procedure allows the derivation of α-effect behavior for both methyl and benzyl transfers from phenylmethyl sulfides and comparison on a quantitative basis. The two sets of correlation lines for Me and Bz transfer are as follows (only direct kinetic rate constants are used):

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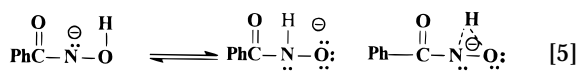
nucleophiles vs Ph S$^+$RMe

Me transfers

(1) NMBH   log k^a_{nuc} = 0.86(0.06)pK_a −11.991

$\qquad$ (LG = PhSMe)

(2) PhO−   log k_{nuc} = 0.452(0.07)pK_a − 7.39

$\qquad$ (LG = PhSMe)

Bz transfers

(3) NMBH   log k^a_{nuc} = 1.11(0.135)pK_a − 13.881

$\qquad$ (LG = PhSMe)

(4) PhO−   log k_{nuc} = 0.70(0.11)pK_a −11.341

$\qquad$ (LG = PhSMe)

for leaving groups (LG) from MeSAr$_2$

Me transfers

(5) log k^a_{nuc} = 0.42(0.03)(−pK_{lg}^{Me}) − 2.26

$\qquad$ (Nuc = 4-ClNMBH anion)

(6) log k_{nuc} = 0.360(0.063)(−pK_{lg}^{Me}) − 1.03

$\qquad$ (Nuc = 3-NO2C$_6$H$_4$O$^-$)

Bz transfers

(7) log k^a_{nuc} = 0.46(0.037)(−pK_{lg}^{Me}) − 0.508

$\qquad$ (Nuc = 4-ClNMBH anion)

log k_{nuc} = 0.061(0.0031)(−pK_{lg}^{Me}) − 0.661

$\qquad$ (Nuc = 3-NO2C$_6$H$_4$O$^-$)

Deriving the α-effect from these correlations for each transfer from both sides leads to equations of the forms of (9) and (10).

$$(9)\ \log k_{nuc}^{\alpha} - \log k_{nuc} = (\beta_{nuc}^{\alpha} - \beta_{nuc})pK_a + C_1$$

$$(10)\ \log k_{nuc}^{\alpha} - \log k_{nuc} = (\beta_{lg}^{\alpha Me} - \beta_{lg}^{Me})pK_{lg}^{Me} + C_2$$

The first set of equations (1−4) defines the α-effect from contributions of the nucleophile side, giving eq 9. The second set (5−8) does the same for the leaving groups, giving eq 10. Differentiation of eqs 9 and 10 to give two equations of the type of eq 11 leads to analysis of the behavior of the α-effect as a function of the log k and β parameters from both the nucleophile and the leaving group sides of the form δα-effect/δpK = β^{α} − β (Differentials of constants are 0.0.). Table 5 summarizes the findings for methyl and benzyl transfers.

$$(11)\ \partial (\log k^{\alpha} - \log k_{nuc})/\partial pK = (\beta^{\alpha Me} - \beta_{nuc})$$

In the NMBH-dialkylphenyl sulfonium system it is clear that the change in the size of the α-effect vs change in pK_a is nearly the same for these NMBH anion nucleophiles no matter which group is transferred. The fact that the α-effect from the nucleophile side responds to electron demand in benzyl transfer, just as it did in

Table 5. ∂ α-Effect/∂pK Behavior in Methyl and Benzyl Group Transfers from MeSAr in Methanol at 30 °C

	$\Delta\alpha$-effect/ΔpK_{nuc} (nucleophiles)	$\Delta\alpha$-effect/ΔpK_{lg}^{Me} (leaving groups)
Me trans	0.43 (±0.045)	0.061 (±0.053)
Bz trans	0.41 (±0.13)	0.40 (±0.049)

methyl transfer, indicates the presence of an electronic effect in benzyl transfer also.

The changes of the α-effect vs the pK_{lg}^{Me} for the leaving group side are also quite instructive. In Figure 2, the α-effect crosses the normal nucleophile line when the leaving group is as poor as MeSPh. This perhaps indicates a validation of our postulate[2] that if the leaving group is not a good one the α-effect is significantly diminished, sometimes not even observable.

Along with that postulate, we proposed that operation of the α-effect depended on donation of a degree of SET character toward the C atom,[9] with subsequent spreading of extra charge throughout the TS structure. Other factors, such as solvent effects, could modify the expression of the α-effect observed, depending on the loci where charge was found. An example of such a possible operation occurs with *p*-MeNMBH anion reacting with *p*-nitrophenylacetate in water−acetonitrile mixtures.[14] The only α-nucleophile to show a substantial change in the size of the α-effect was *p*-MeNMBH anion as the mole percent of MeCN increased. The α-effect for *p*-MeNMBH was 42 (k^{α}_{nuc}/k_{nuc}) at 0% MeCN and 1188 at 90% MeCN. The point at which the *p*-MeNMBH became the dominant nucleophile was ca. 45% MeCN. It is worthwhile to suggest that the NMBH-type-α-nucleophiles, which do not have the additional chance to ionize from N instead of O, as hydroxamates do, have lower reactivity in aqueous phases than the hydroxamates. This lower activity may be because the NMBH anion nucleophiles lack the internal base catalysis associated with the benzohydroxamates[12] in S_N2 reactions and reactions at the carbonyl group ([5]). The NMBH anions α-effects are not as large as hydroxamates until solvent conditions approach those that favor addition of the Me-N−O⁻ to the C=O bond, by stabilizing excess charge transfer to the carbonyl O atom, causing the O⁻ of the adduct by to be stabilized efficiently by H bonding to small amount of solvent water molecules (but with less solvation of the N−O⁻ charge). With larger amounts of water it is plausible that addition of water to the C atom also competes with the *p*-MeNMBH anion, but not the benzohydroxamate ion, because of the internal base catalysis. The operation of benzohydroxamate in giving lower α-effects than NMBH anion at ca. 45% MeCN might be considered as no proton transfer to CH₃N as in [5], due to less solvent promotion of this transfer with greater MeCN content.

$$\underset{\ddot{\text{O}}}{\overset{\overset{\displaystyle O}{\|}}{PhC}}-\overset{\overset{\displaystyle H}{|}}{\underset{..}{N}}-\overset{\ominus}{\ddot{\text{O}}}{:} \quad \Longleftrightarrow \quad \underset{..}{\overset{\overset{\displaystyle O}{\|}}{PhC}}-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\ominus}{\ddot{\text{O}}}{:} \quad Ph-\overset{\overset{\displaystyle O}{\|}}{C}-N\overset{\ominus}{\underset{..}{O}}{:} \qquad [5]$$

This idea of internal base catalysis is reported to be responsible for the benzohydroxamate α-effect. Although this idea is known from the early days of the α-effect[12] with this hydroxamic acid chemistry, and although [5] is considered by ref 14, it seems not to play a great part of the explanation for the large variation of the α-effect

Table 6. Comparison of LFER Parameters for Methyl and Benzyl Transfers between Nucleophiles

nucleophile	group	leaving group	β_{nuc}	β_{lg}^{Me}	apparent total bond order[a]
NMBH	Me	⁻O₃SAr	0.86	0.44	1.42[2]
phenolate	Me	⁻O₃SAr		0.46	
NMBH	Me	MeSAr	0.85	0.42	1.43
phenolate	Me	MeSAr	0.31	0.54	0.76
	Bz	MeSAr	1.11	0.46	1.65
phenolate	Bz	MeSAr	0.66	0.09	1.57

[a] Calculated from $\beta_{nuc} + (1.0 - \beta_{lg}^{Me})$.

with solvent composition for these workers. In fact, their conclusion was that ground-state solvation was not solely responsible for the α-effect they observed, which is at least consistent with our hypothesis that an intrinsic α-effect exists with C atom transfer, and that effect is modified by changes in the type of C atom in the simple CH₃ group.

The data in the present system indicate that the LFER (linear free energy relationship) parameters do not adequately describe the transition state. We have previously[2−4] described methyl transfers to NMBH anions from arylsulfonates and methylaryl thioethers in terms of β_{nuc} and β_{lg}Me. The results of these studies are presented for comparison with the present data in Table 6.

Clearly, the data in the present study gives apparent bond orders that no More O'Farral−Jencks diagram can accommodate. The methyl transfers fit on such a diagram, allowing agreement with Buncel's [16] suggestion that the α-effect gives a tighter TS by an anti-Hammond motion away from the concerted reaction coordinate. No such analysis is possible when we are certain of a β^{α}_{nuc} greater than 1.0.

Marcus has demonstrated a mathematical explanation for unusual slopes of linear free energy plots in kinetics.[17] When a group, Y, in a reactant is varied, both $\Delta G°$ and the intrinsic term, $\Delta G_{int}^{\ddagger}$, change. The slope of the free energy plot, from the form of the Marcus equation is

$$\beta = 0.5(1 + x) + (1 - x)^2 \beta_1$$

where $x = \Delta G°/4 G_{int}^{\ddagger}$ and $\beta_1 = [d\Delta G_{int}^{\ddagger}/d Y]/[d\Delta G°/d Y]$.

The position of the TS along the reaction coordinate is given by $0.5(1 + x)$. Only when $d\Delta G_{int}^{\ddagger}$ is constant for a reaction series does β map the distance along the reaction coordinate. In the present benzyl transfer to NMBH anions from MeSAr it is possible that a change in $d\Delta G_{int}^{\ddagger}$ because of transfer of excess charge to the benzyl group occurs.

As an example, consider a series of closely related reactions where the conditions of the Marcus suggestion are met. Suppose the transition state for some nominal reaction within the series occurred at $X = 0.5$ along the reaction coordinate. Then, because of the square term in the Marcus expression, the observed β would be 1.00. Only a slight increase toward the product along the concerted reaction coordinate would result in a β larger than 1.00.

The fundamental SCD idea in Figure 5 is that the wave function at the avoided crossing in the transition state is made from the valence bond (VB)(**A**−**D**) contributions below.[6,8] In the present case, added amounts of **D** would change the degree of solvent reorganization in the TS.
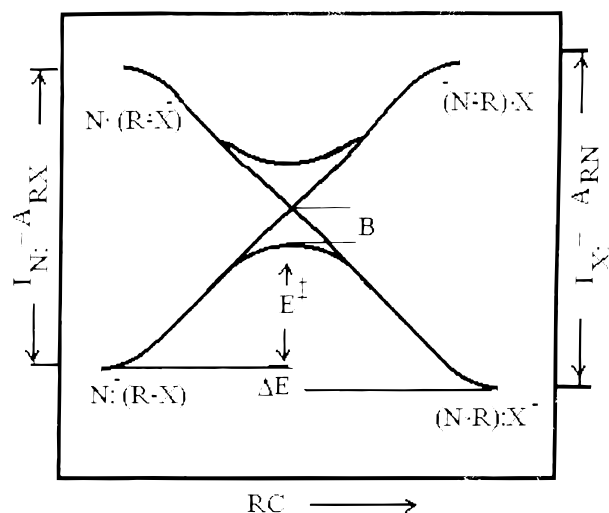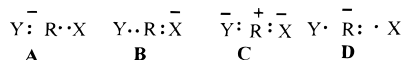
Figure 5. SCD model of reactivity.

(especially important in consideration of reaction [4] as having a neutral species at the transition state).

Contributions of **A**−**C** are all solvent dependent; if the substrate R−X is positively charged, then only **D** is neutral. The degree to which Y:⁻ can transfer SET charge character will largely determine how much **D** is mixed into the TS wave function, and how much of the SET can be placed on X in the TS will also be important. These considerations fit the data presented in this paper quite well.

An explanation of the change of sign of the slopes in Figure 4 of the size of the α-effect vs ELUMO of the electrophilic salt from negative for methyl transfer to positive for benzyl transfer is available using these models. The modification of the transferring C atom to the benzyl case involves contributions such as **D′**, because any amount of transfer of SET character makes the wave function resemble a neutral species. This weakening of the S⁺−C bond by SET transfer is consistent with both the reported electrochemistry[5] and the increasing stabilization of the ELUMO leaving group component of the α-effect for SET transfer.
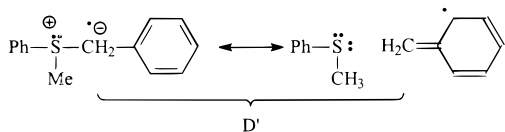

The methyl transfer line in Figure 4 has a negative slope, opposite to that for benzyl transfer, indicating that in this case the ability to express the α-effect for the leaving group is lessened by acceptance of SET character. An explanation of these two slopes comes from the SCD model.[8b] The benzyl transfer case is easiest to explain in the normal sense of stabilization of negative or single-electron character The benzyl transfer possibly involves contributions such as **D′**, because any transfer of any SET character makes the sulfonium salt resemble a neutral species even more. This weakening of the C−S bond by SET transfer is consistent with the positive sign of the slope for benzyl transfer in Figure 4. The methyl group

transfer has a negative slope in Figure 4, implying that any receipt of SET character actually hinders the expulsion of the leaving group, aryl methyl thioether.

If some SET character is transferred during the formations of both methyl and benzyl transition states, then the degree of contribution to the α-effect due to expulsion of the leaving group depends on how the transferred SET character stabilizes or weakens the S−C bond. The role of delocalization of charge or spin into the benzyl group is realized in the discussion above, but just how the CH₃ group could both accept SET character and stabilize the S−C bond is not clear. Most likely delocalization of spin into the C−H bonds is the only mechanism of stabilization available. Thus, most spin remains on the C atom.

A potential explanation comes from electrochemical reductions of sulfonium ylides. Electrochemical oxidation of sulfonium ylides produce very stable radicals. The radical stabilizing effects of S⁺ are explained by **D″**, as a three-electron-two orbital bond.[9,18]
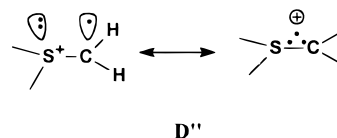
The merit of this model for the present data is that some **D″** character would likely mix into the wave function for the transition state for methyl transfer because the delocalization of spin into the C−H bonds is not extensive, and there is more spin density available on the C atom to participate in the three-electron bonding between S and C. Stabilizing the receipt of SET character with the substitution on the aryl group of the MeSAr leaving group can thus actually lead to strengthening the bond to the leaving group, if the SET character is localized, or weakening the bond to the leaving group if the SET character is delocalized into the group being transferred.

Other possible explanations are not as attractive. Solvent effects as a root cause of the α-effect might be invoked if the benzyl transfers were also to involve more open transition states, susceptible to greater solvent interaction, i.e., greater mixing of **C**. This plausible idea is rendered less so by considering the above, where charge is actually diminished in the TS for both the normal and α-nucleophiles and the substrate. It is hard to see how solvent effects could change the sign of a plot of the size of the α-effect vs the SET parameter, −ELUMO if the entire α-effect were due to solvent effects.

Conclusion

The size of the α-effect depends on the ability of the nucleophile to transfer SET character, the group being transferred, the ability of the leaving group to conduct excess charge away from the TS, and the ability of the group being transferred to weaken or strengthen the bond to the leaving group.