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The α-Effect in Methyl Transfers from *S*-Methyldibenzothiophenium Fluoroborate to Substituted *N*-Methylbenzohydroxamates

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Studies of the α-effect show increased reactivity of nucleophiles having lone pairs of electrons on atoms neighboring the lone pair involved in reactivity when compared to the basicity of the nucleophiles. Hammett-type plots and Brönsted-type plots of substituted methylphenyl sulfates vs hydrogen peroxide anions and substituted *N*-methylbenzohydroxanates (NMBH) with substituted methylarenesulfonates or substituted arenedimethylsulfonium ions have large ρ or β_{nuc} values, indicating a putative tightening of the usual S_N2 transition states (anti-Hammond effect). Electrochemical studies of S_N2-SET or reactivity indicate that SET character occurs in looser transition states, whereas S_N2 transition states are associated with greater tightness. The α-effects for the series of sulfonium salts in completion reactions for 3-ClNMBH anions and 3-nitrophenolate anions are (log k_α/k_{normal}) 1.124 for dimethylphenyl sulfonium, 1.512 for dimethyl-1-naphthyl sulfonium, 1.835 for dimethyl-9-anthracenyl sulfonium, and 1.137 for *S*-methyldibenzylthiophenium. Correlations of the sizes of α-effects with typical SET (or ET) experimental parameters and the inverse dependence of the size of the α-effect on electron demand indicate inclusion of SET character in these S_N2 transition states, vs no (or at least diminished) SET character in normal transition states. This dichotomy of tighter S_N2 transition states, but looser SET transition states indicated in the α-effect, is examined in the present work.

Introduction and Background

The α-effect is an enhanced nucleophilicity of a nucleophile, compared to its basicity, that has a lone pair of electrons on an atom next to the pair of electrons undergoing nucleophilic attack. Structure **1** shows a

X-Y

1

stylized α-nucleophile. The phenomenon of the α-effect has puzzled chemists since it was first observed over forty years ago.[1−5]

Classical physical organic chemistry studies over the last fifteen or twenty years have yielded some important clues about the nature of the α-effect. Buncel's group, in a series of papers[6,7] studying methyl group transfers from substituted phenyl sulfates to the α-nucleophiles hydrazine and HOO^- anion, have concluded that these S_N2 reactions show a tightening of the transition state (TS) (an anti-Hammond effect). Subsequently our group showed an α-effect transferring methyl groups from substituted arenesulfonates to substituted *N*-methylbenzohydroxamate anions (NMBH anions)[8] likewise showed larger β_{nuc} (slope of a Brönsted-type plot), hence indicating anti-Hammond tightening of the S_N2 TS. A correlation of the rates of nucleophilic substitution with oxidation potentials of the substituted NMBH anions suggested that the α-effects observed were at least partially due to inclusion of some single electron character (SET) in the S_N2 transition states. A correlation with pK^{Me}_{lg} values[24] also

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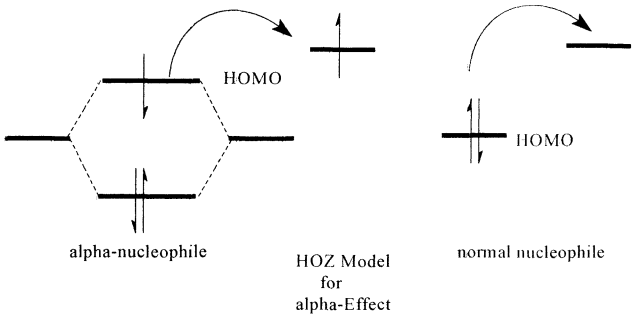

FIGURE 1. The Hoz model for the α-effect.

indicated a tighter than usual transition state occurred in these methyl transfers, hence also in the α-effect.

Figure 1 shows a model proposed by Hoz[9] for the α-effect that suggests inclusion of some SET character in the S_N2 transition state, as in the postulated S_N2 model of Shaik and Pross.[10,11] The normal S_N2 reaction is shown as the "polar" model. Can this α-effect model be compatible with the observed Brönsted-type slopes putatively showing tighter transition states accompanying the α-effect?

We have shown from studies of methyl group transfers[12−14] and benzyl group transfers[15] from substituted aryldimethysulfonium ions to substituted *N*-methylbenzohydroxamate anions (NMBHO$^-$) that the transition states in reaction I are both tighter, from Brönsted-type

$$G_1C_6H_4CON(Me)O^{\ominus} + CH_3{-}\overset{\oplus}{\underset{\displaystyle Me}{S}}{-}C_6H_4G_2 \longrightarrow G_1C_6H_4CON(Me)OCH_3 + MeSC_6H_4G_2 \quad \textbf{(I)}$$

plots of log k_{nuc} values vs pK_{nuc} and correlations of pK^{Me}_{lg}.[14,24] The α-effects also correlate with typical SET parameters (such as IP of the nucleophiles or reduction potentials of the sulfonium salts) implying the size of the α-effect is connected to some SET transfer in the S_N2 reaction.

Both methyl and benzyl group transfers respond to increasing electron demand in the α-nucleophiles, showing that the α-effect responds to an electronic effect. This means, at least partly, that the α-effect is electronic in these systems.

The present state of affairs is apparently one where the α-effect, at least in transfers from methylarene sulfides, is partly caused by some SET character in the transition state in an S_N2 reaction, and this transition state is tighter than that for a normal S_N2 reaction.

Lund[16−18] et al. and Bordwell[20] have shown by electrochemistry that in a system of SET-S_N2-type the SET character is more dominant in an open (looser) transition state. If the α-effect is due, at least partly, to an electronic effect that includes some SET character, then it is reasonable to expect a diminished α-effect where the transition state is less open.

A brief description of that electrochemical work is instructive. Using radical anions, ArH$^{\bullet-}$, and the carbanion generated electrochemically from 4-(methoxycarbonyl)-*N*-methyl pyridinium iodide, Lund and Kristensen[16] observed outer-sphere SET substitutions for the reaction with *t*-BuBr, and similar substitutions with 1-adamantyl and neopentyl bromides. Butyl bromide and 2-butyl bromide appeared to react by borderline SET-S_N2 reactions.[16,17] Recently the problem has been cast in terms of TS tightness,[21] with an S_N2 TS tighter than the SET TS. Additionally, these workers report that there is a gradual change from the characteristics of a pure SET reaction to those of a classical S_N2 reaction from studies of activation parameters as well as kinetic ($k_{SUB}/_{SET}$) studies, as well as stereochemical studies. These workers admit that competition between outer-sphere dissociative, SET (followed by radical coupling), or a classical S_N2 route may be operating. By studying the linear dependence of lnk vs T^{-1} they suggested no such shift in reaction.

A contrasting view is expressed by Sørensen and Daasbjerg,[19]using such radical anions as anthracene radical anion and a series of alkyl halides, and trimethylsulfonium fluoroborate. These workers employed an analysis using a parameter $q = [R^-]/[RA^-] + [R^-]$ in the set of eqs 1−6 (included in the following quotation) to suggest that a q value dependent on the nature of the halogen atom, X, would be consistent with the presence of an S_N2 component, whereas a constant q value would suggest a pure SET mechanism. The dimethyl sulfide leaving group gave a pure SET mechanism (!), whereas the methyl halides showed increasing S_N2 percentages in the order Cl > Br > I. The order was the same for butyl halides. The authors state that: "...one would expect the transition state to occur later as the electron acceptor becomes poorer, with a diminished distance between the radical anion and the electron acceptor as a consequence. Ultimately, such a situation should favor the bonding interaction in the transition state and thus the S_N2 mechanism overall in agreement with the actual development observed in the results reported herein."

ET (1)

$$A^{\bullet-} + RX \xrightarrow{k_{ET}} A + R^{\bullet} + X^- \quad (1)$$

$$A^{\bullet-} + R^{\bullet} \xrightarrow{k_2} RA^- \quad (2)$$

$$A^{\bullet-} + R^{\bullet} \xrightarrow{k_3} A + R^- \quad (3)$$

S_N2

$$A^{\bullet-} + RX \xrightarrow{k_{S_N2}} RA^{\bullet} + X^- \quad (4)$$

$$A^{\bullet-} + RA^{\bullet} \xrightarrow{k_5} RA^- + A \quad (5)$$

Total (ET + S_N2):

$$2A^{\bullet-} + RX \rightarrow (1 - q)RA^- + qR^- + (1 + q)A + X^- \quad (6)$$

Recently Costentin and Savéant[22] have shown, from ab initio UMP2 level computations, that the looseness of the transition state of system NO$^-$ reacting with RCl favors the SET reaction, implying the same conclusion, i.e., S_N2 transition states are tighter than SET transition states. This agreement from several approaches seems to indicate that SET is favored from open transition states, while S_N2 transition states are more closed, or tighter.

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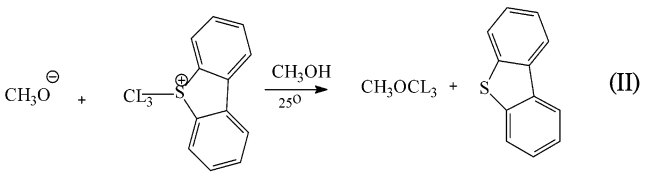
To sum up, the expectation is that the looser transition states in either an SET-S_N2 continuum model or competing SET-S_N2 model favor SET. The tighter the TS in either model implies greater S_N2 character.

The α-effect studies with sulfonium salts to date seem thus to have a contradiction in them if slopes are used as indices of tightness. The TS s from simple kinetic studies appears to be tighter than normal S_N2 reactions from the slopes of Brönsted-type plots (β_{nuc} values) for both the incoming nucleophile and the leaving groups. Yet their reaction rates correlate quite well with SET parameters, such as oxidation and reduction potentials. One could easily ask the following question: Do the very large β_{nuc} values (0.85−1.2) refer only to excess *charge* transferred in the α-effect transition states due to SET character in looser S_N2-type transition states, thus retaining the feature of looser transition states for inclusion of SET character, or are the α-effect transition states simply tighter than normal S_N2 reaction, corresponding to anti-Hammond changes?

It would be interesting to study an S_N2 substrate known to have a well-characterized transition state of the same charge type as aryldimethylsulfonium ions, with a strong nucleophile, reacting with an α-nucleophile to examine the changes in reactivity and transition state with expression of an α-effect. Such a substrate has been reported by Schowen et al.[23] in reaction II.



2

The *S*-methyldibenzothiophenium ion, **2**, allowed the secondary kinetic isotope effect value (SKIE) to be determined (SKIE = 0.974 ± 0.016) with L = H, D, and a primary kinetic isotope effect with ^{13}C (=1.083 ± 0.015).[23] From these data it was suggested that the TS for (II) has a "symmetrical" structure, with the methyl group planar and the C−O and C−S bond orders of similar magnitude. These authors also undertook to classify representative SKIEs of a large number of known S_N2 reactions and related them to transition-state fractionation factors (φ_T). The SKIE of (II) was in the range of a normal S_N2 transition state, and the φ_T analysis placed (II) in the normal range for an S_N2 reaction.

The present paper reports the results of reaction III, wherein the reactions of **2** with Nuc: being both substituted *N*-methylbenzohydroxamate anions (G_1NMBH anions) and substituted phenolates ($G_2C_6H_4O^-$) in methanol at 30 °C were run. The questions to answer from this study are the following: (1) Is an α-effect present? (2) Does the α-effect change the essentially "normal" S_N2 character of the transition state? (3) Is the SKIE of reaction III comparable to the SKIE of reaction II with the Nuc: an α-nucleophile? Questions 1 and 2 are the subjects of this paper. Question 3 will be the subject of a future paper.

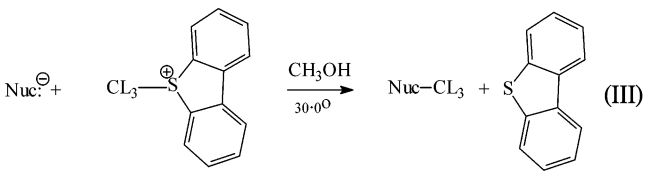


TABLE 1. Summary of Competition Reactions of GNMBH Anions and Gphenolates with *S*-Methyldibenzosulfonium Cation in Methanol at 30.0 °C

	k_{rel}(SD)		
nucleophile	GCMS	^{1}H NMR	pK_a
G-NMBH anion			
H	13.7(0.20)		12.38
4-Cl	7.31(0.56)		12.04
4-NO_2	3.70(0.30)	3.00(0.50)	11.5
4-Me	12.94(4.7)	9.12(1.00)	12.45
4-MeO	23.50(2.53)	21.26(1.25)	12.80
3-CF_3	3.93(0.55)		11.83
G-phenolate			
3-NO_2	1.00		12.44
4-NO_2	0.50(0.02)		11.50
4-CN	0.869(0.099)		12.31
3,5-Cl_2	1.182(0.011)		12.60
3,4-diCl_2	1.36(0.05)		12.98
4-CHO	0.688(0.25)		12.01
4-MeO	6.19(2.53)		15.04

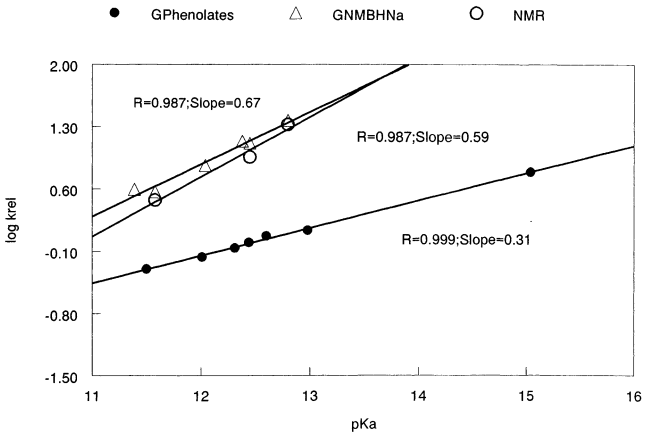


FIGURE 2. Brönsted-type plots for GNMBH anions vs gphenolate in methanol at 30.0 °C.

Experimental Section

The *S*-methyldibenzothiophenium (SMPT) fluoroborate salt was made analogously to the aryldimethylsulfonium salts by heating trimethyloxonium fluoroborate with dibenzothiophene in dichloromethane.[23] The H NMR in acetone-d_6 was clean and entirely consistent with the salt. Its melting point agreed with the reported compound[13](mp 150−151 °C).

The relative rates for the phenolate anions reacting with **2** cations are given in Table 1, and plotted in Figure 2 as Brönsted-type plots of log k_{rel} vs pK_a of the conjugate acid of the nucleophiles. A typical run is given as shown in the next section on GCMS. Likewise, the k_{rel} values of the G-NMBH anions were determined and summarized in Table 1. Three k_{rel} values of G-NMBH anions were verified by H NMR, also in Table 1.

Competition Reactions of Phenolates and G-NMBH Anions Reacting with *S*-Methyldibenzothiophenium Fluoroborate. Determinations by GCMS. A solution of 0.5 mmol of both sodium 4-nitrophenolate and sodium 4-nitrophenolate was made in 4.0 mL of absolute methanol. The solution was thermostated in a waterbath at 30.0(± 0.1) °C

for 15 min. A sample of 0.026 mmol of fresh **2** fluoroborate was placed in the methanolic sample and allowed to stand for 3 h at 30 °C. The **2** fluoroborate salt dissolved immediately in the solution. After 3 h a gcms sample was introduced into the inlet of the GC equipped with an MSD that we have previously used for our work.[8,13−15] The column was a methylsilicon gum cross-linked capillary (12 ft × 0.33 μm). Analysis of the MS and results was obtained on software supplied with the GCMS. This system was previously[8] found to be linear in grams (±5%) for samples determined on it. The k_{rel} was obtained by the ratio of integrated areas of the methyl products of the reactions, adjusted where appropriate by ratios of molecular weights. The k_{rel} values for the other phenolate anion were determined similarly. The results are summarized in Table 1, and plotted in Figure 2.

The lower line in Figure 2 shows the goodness of fit for the plot of the phenolates (R = 0.999). The last point on the line at 15 pK_a units was obtained by competition of 4-methoxyphenolate vs 4-methoxyNMBH anion that was already determined vs 3-nitrophenolate anion. Correction for the k_{rel} of the 4-methoxyNMBH anion gave the point for 4-methoxyphenolate on the phenolate line. The topmost line of Figure 2 shows the G-NMBH anion line. This inverse extrapolated point gave us a measure of the validity of the pair of lines for the phenolates and the G-NMBH anions because, apparently, one line would predict points on the other line.

Determinations of k_{rel} for G-NMBH Ions. Analysis by GCMS. Competition reactions with both G-NMBH and 3-nitrophenolate were set up as for k_{rel} for the phenolates, as above. After an initial line was established (topmost in Figure 2) selected points were verified with competitions with nearly pK_a matched phenolates.

The identities of the G-NMBHOCH$_3$ peaks on the gc trace were verified as previously reported,[3] by spiking samples of the reaction mixtures with authentic material. In some cases small amounts of impurities overlapped the areas of the desired product peaks, and had to be eliminated by a manual integration routine, supplied by the software. A line was dropped connecting the point of intersection of each impurity with the known peak with the baseline by means of the mouse pointer. This line was extended along the baseline until the known peak joined the baseline and the areas were recorded digitally. This somewhat-less-than-optimum method of determining the areas gave the triangular points on the top line of Figure 2. The scatter is apparent by looking at the figure. We thought it necessary to validate this line because of the difficulty in obtaining the exact areas of small peaks on the gc. The next section gives the attempt at validation by HNMR.

Determinations of k_{rel} for G-NMBH Anions vs 3-nitrophenolate and 4- Nitrophenolate Anions via HNMR. Several G-NMBH anions were allowed to compete with 3-nitro- and 4-nitrophenolate ions in methanol-d_4. The HNMR spectra were obtained after concentrating the solutions to ca. 2−3 mL. Integral traces were obtained digitally for the products. The three clearest points (no overlapping peaks) were taken as indicating the k_{rel} by this method. These values appear as circles in the middle line of Figure 2, and as ^{1}H NMR in Table 1. The NMR has been described previously.[8]

Determination of the Reduction Potentials of *S*-Methyldibenzothiophenium Fluoroborate, Phenyldimethylsulfonium, 1-Naphthyldimethylsulfonium, and 9-Anthracenyldimethylsulfonium Fluoroborates. These parameters were obtained in acetonitrile, as previously reported for the aryldimethylsulfonium fluoroborates.[14] The values were 1388 mV for *S*-methyldibenzothiophenium, 957 mV for phenyldimethylsulfonium, 1252 mV for 1-naphthyldimethylsulfounium, and 1528 mV for 9-anthracenyldimethylsulfonium. The standard errors in all were ±5 mV.

These values were obtained by cyclic voltammetry, using acetonitrile solutions containing 0.05 M tetrabutylammonium tetrafluoroborate, at a sweep rate of 100 mV/s with an Ag/AgCl electrode and 5 nM ferrocene as an internal standard. The potentials are corrected to the SCE electrode.

Computational chemistry was performed by Hyperchem v. 5.5 or v. 6 on Gateway computers operating Windows 98 at 366 or 400 mHz. The methyl cation affinity (MCA) and the methyl radical affinity (MRA) of dibenzothiophene were computed as reported for aryl methyl sulfides.[13] The values were (PM3) −97.80 eV for MCA and −16.49 eV for MRA.

Results

The kinetic data from reaction III are summarized in Table 1, and plotted in Brönsted-type plots in Figure 2. The slopes of the two α-effect plots by GCMS and HNMR are very similar, thus the data are at least internally consistent. The sizes of these slopes are both smaller than those reported for GNMBH anions reacting with aryldimethylsulfonium ions.[14] This β_{nuc} value was reported as 0.85, with a β_{lg}^{Me} value[14] of 0.42.

Comparison of these β_{nuc} values indicates that GNBMH α-nucleophiles in reaction III transfer less charge than in the reaction of GNMBH anions with substituted aryldimethylsulfonium ions. In reaction III the slope for the substituted phenolates is about that for substituted phenolates reacting with methyl-substituted benzenesulfonates (0.31),[8] whereas for the substituted aryldimethylsulfonium case it was 0.45. Both values are in the normal range for a normal S_N2 reaction.

From these data we obtain the result that reaction III with α-nucleophiles is more like a normal S_N2 reaction than methyl transfers from substituted aryldimethyl sulfonium ions. However, an α-effect of about 1.137 (logk_α − log k_{normal}) is still expressed. This α-effect is greater than any expressed in the substituted aryldimethylsulfonium case (0.222 to 0.926),[12] but considerably smaller than α-effects from 1-naphthyldimethylsulfonium (1.512), or 9-anthracenyl (1.835).[13]

The response of the α-effect to electron demand can be determined by subtracting the regression equation for Brönsted-type plots for substituted *N*-methylbenzohydroxamates from the regression equation for the normal nucleophiles (phenolates) and differentiating the result to get ∂ α-effect/∂ pK_{aH} = ($\beta_{(nuc;\alpha-nucleophile)}$ − $\beta_{(nuc;normal\ nucleophile)}$).[15] It is worthwhile noting that the response of (III) to increasing electron demand in the α-nucleophiles (GNMBH) is less for (III), 0.586−0.309 = 0.277, than for the substituted aryldimethylsulfonium case, 0.43.[15]

Plotting the size of the α-effect vs the reduction potentials gives Figure 3. The regression coefficient for the three aryldimethylsulfonium reaction with 3-nitrophenolate vs 4-ClNMBH, determining the α-effect, shows a very good fit for the three aryldimethylsulfonium ions implying that these three ions are of the same type of dependence on the SET parameter. There is a much different dependence for (III) on the SET-type parameter. The size of the α-effect is more like the phenyldimethylsulfonium value than like a sulfonium cation between the 1-naphthyl and 9-anthracenyl cases as would be expected from the size of the reduction potential.

Discussion

The expectation that reaction **III** would give less α-effect than with aryldimethyl sulfonium ions is not

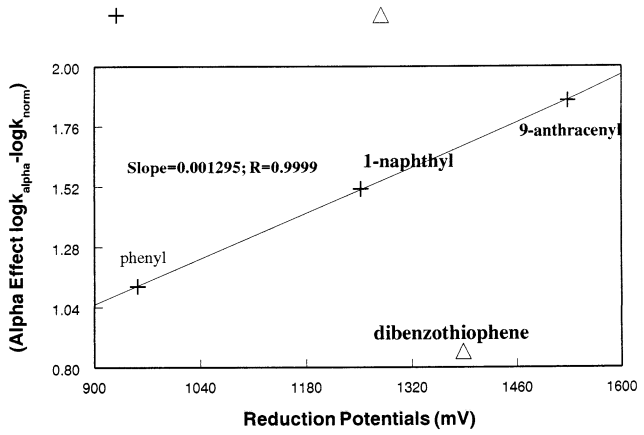


FIGURE 3. The reduction potentials of arenyldimethylsulfonium ions and *S*-methyldibenzothiophenium ion vs the size of the α-effect.

quite fulfilled. The α-effect in (III) is approximately the same as that for phenyldimethylsulfonium ion when the α-effect is determined by competition between 3-nitrophenolate ion and 4-ClNMBH ion (1.124).[13] However, the phenyldimethylsulfonium ion least readily accepts a single electron in the series phenyl, 1-naphthyl, 9-anthracenyl.[25] There is thus a clear disconnect between the size of the α-effect in the two series from the standpoint of SET-type parameters, such as reduction potentials. This implies that reaction III transfers less SET character than reaction II.

The methyl cation affinity of dibenzothiophene at a PM3 level of theory is less than the value for thioanisole[13] (−97.8 eV vs −99.11 eV), indicating a less stable *S*-methyl group by 1.31 eV. Likewise, the methyl radical affinity, −16.5 eV, is less than the thioanisole value by 1.6 eV. These numbers indicate that transfer of the methyl group from **2** ought to be more thermodynamically favored than that from the S atom of phenyldimethylsulfonium cation. An interpretation of these results might indicate that the pair of electrons on S in *S*-methyldibenzothiophenium cation becomes part of an aromatic system upon methyl group transfer, whereas the pair of electrons in phenyldimethylsulfonium cation does not.

Some support for this interpretation is available from the literature. For example, comparing the pK_{aH} values of 9-methylanthracene (=27.7 in MeOH-DMSO)[26] and fluorene (=20.5 in MeOH-DMSO)[26] shows a $10^{7.2}$ difference in the ability of these systems to support a pair of electrons on carbon. An analogous amount of stabilization of S electrons would give a stabilization energy of ca. 10 kcal. This large stabilization energy indicates, perhaps, that a key element in the reaction of **2** with 4-ClNMBH anion is transferring a pair of electrons into an aromatic system, whereas in the aryldimethylsulfonium cases the pair of electrons ends up in a nonaromatic situation.

If this line of reasoning is acceptable, then the present result that an α-effect is retained in reaction III needs to be explained because the process of displacing a pair of electrons from the CH_3 group to a leaving group is an essentially S_N2 feature. As we have seen in the Introduction, the putative SET character of the α-effect in aryldimethylsulfonium reactions would require a looser, not a tighter, S_N2-type TS. The smaller β_{nuc} for **2** reacting with the α-nucleophiles compared to the aryldimethylsulfonium case indicates, from this criterion only, a looser S_N2 TS in this "normal S_N2" substrate than for the aryldimethylsulfonium series.

A reconciliation of these observations can be effected if the slopes of Brõnsted-type plots are interpreted as indicating only the amount of charge transferred in the TS, and not necessarily indicating a tightening of the TS. Detailed geometry studies, such as secondary kinetic isotope effects with labeled Me groups, primary kinetic isotope effects, labeling the C atom, or high-level ab initio results, would be a better indicator of the TS geometries if this reasoning is correct. Such studies are presently underway in this laboratory.

If these results are accepted, it is easy to fit them into the Shaik and Pross S_N2 model.[10,11] The lowest four valence bond (VB) configurations of an S_N2 TS are shown in eqs 1−6. The total wave function for the TS will be

$$\Psi = a\varphi_a + b\varphi_b + c\varphi_c + d\varphi_d \qquad \text{(IV)}$$

In the aryldimethylsulfonium reaction with an α-nucleophile, eq IV, the stronger dependence on SET-type parameters for the α-effect indicates the weighting coefficient, *d*, is greater than it is for reaction III when Nuc: is a normal nucleophile.

Conclusions

The smaller α-effect in eq III and the smaller β_{nuc} for α-nucleophiles and phenolates compared to eq I indicate less charge transfer in the TS for eq III. The question of comparative tightness of the S_N2 transition states for the two reactions cannot be totally answered from the slopes of Brönsted-type plots alone. It is clear that the "normal" S_N2 transition state in eq III is changed less than the S_N2 transition state in reaction I when the reaction involves α-nucleophiles.

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