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Evidence That the α-Effects in Methyl Transfers from Aryldimethylsulfonium Salts Correlate with Single-Electron-Transfer Characteristics

K. R. Fountain* and Kamlesh D. Patel

Truman State University, Kirksville, Missouri 63501

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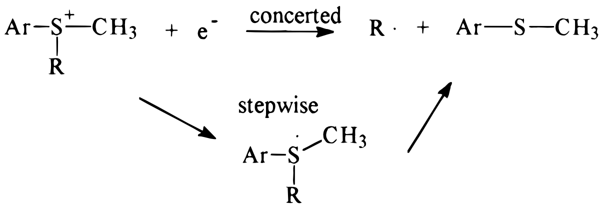
The ability of the anions of *N*-methylbenzohydroxamic acids to demonstrate the α-effect in methyl transfers from aryldimethylsulfonium salts correlates with the ability of these salts to demonstrate single-electron (SET) character in electrochemical experiments.

Introduction

Recently, attention has been refocused on the role of single-electron-transfer (SET) character in wave functions of S_N2 transition states, as predicted by Shaik et. al.[1] Examples of experimental approaches used to demonstrate such SET character in an S_N2 reaction include an early report by Ashby[3a] where radicaloid intermediates in reactions putatively typical of S_N2 classical reactions exhibited large amounts of inversion of configuration. A more recent demonstration of this effect was reported in the identity reaction[2] of bromide ion with *p*-$BrC_6H_4COCH_2Br$ in cumene.[3b] This reaction gave results consistent with disclosing the SET character by trapping radicals in the identity reaction because substantial yields of *p*-$BrC_6H_4COCH_3$ were obtained. The scheme that rationalizes this behavior involves abstracting a hydrogen atom from cumene, present in large excess as the solvent, by the $Br^{\bullet}$ radical component.

An alternate experimental design is possible where the ability of a substrate to accept an electron is correlated with a nucleophile having, at least theoretically, the possibility of donating an electron. Aryldimethylsulfonium salts have recently been shown to be substrates capable of receiving various degrees of SET character in electrochemical experiments.[4,14] The order of increasing ability to undergo SET in these substrates, eq 1, is aryl = phenyl < 1-naphthyl < 9-anthracenyl. Although all the experiments are actually EC type, where electron capture (E) precedes expulsion of a radical (C), the timing of the E steps and the C steps becomes closer (concertedness of the capture of the electron and the expulsion of the radical) in the order 9-anthracenyl < 1-naphthyl < phenyl (i.e., the system takes more character of the top reaction in eq 1 in the phenyl case).



[1]

Factors that promote greater concertedness in this sequence (synchronous capture of the single electron and expulsion of the group) of alkylating agents include weakening of the bond between S and the departing group, implying that the phenyl $S^+{-}CH_3$ bond is the weakest in the series. We will show below that this is not decisively so. An alternative to this bond weakening would be formation of a bond to the departing group by another nucleophile, such as in an S_N2 reaction. Such a possibility would lower the energy necessary to expel a group from the S atom. This set of salts allows us to study nucleophilic attack and to form conclusions about the degree of SET character in methyl transfers when $R{=}CH_3$.

It should be possible to investigate SET transfer from nucleophiles to such substrates. The significance of this strategy is that a theoretical model for the α-effect can be tested. Hoz proposed that the α-effect, displayed by nucleophiles possessing a pair of electrons neighboring the reacting pair (as in hydrazine) reacting at the C=O group, results from SET character in the wave function of the transition state[10] (TS), Figure 1. The wave function of the TS includes this SET character because the transfer of some SET character from an interaction of the four electrons in the α-nucleophile would produce stabilization of the three-electron character. The resulting three-electron splitting contribution is mixed into the wavefunction of the TS in a stabilizing way that accounts for a diminished E_{act} for this reaction.

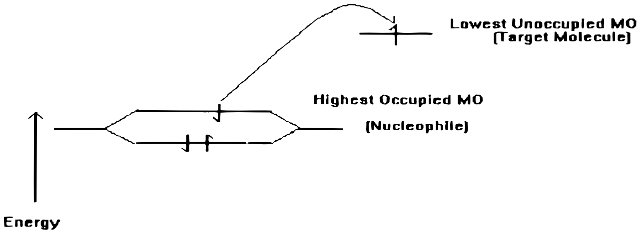


Figure 1. Hoz model for the α-effect.

The α-effect results in increased nucleophilic reactivity compared to a nucleophile having no α-electrons but of the same pK_a value as the α-nucleophile.[5] Buncel as well as our group have both determined that α-effects occur in methyl transfers from sulfates[6] and sulfonates[7] with

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* To whom correspondence should be addressed. Phone: (816) 785-4633. FAX: (816) 785-4045. E-mail: SC18@truman.edu.

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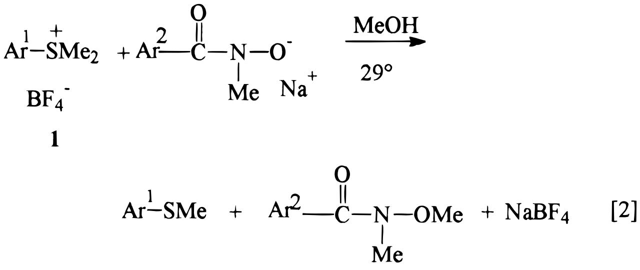
Table 1. α-Effects in the ArS^+Me_2 System in Methanol by Competition Experiments at 29.5 °C

aryl	α-effect
phenyl	13.3 ± 2.5
1-naphthyl	32.5 ±12.0
9-anthracenyl	68.4 ± 14.0

hydrogen peroxide anions, *N*-methylbenzohydroxamate anions (NMBH), and *N*-phenylhydroxylamines (NPHA). Typical ranges for these α-effects are 2.5−11, expressed as a ratio of rate constants, $k_{\alpha-\mathrm{nuc}}/k_{\mathrm{nuc}}$.

We now report that the α-effect demonstrated in methyl transfers from aryldimethylsulfonium salts in eq 1 with NMBH anions (reaction 2) correlates with the ability of the substrates to accept an electron.



Experimental Section

The experiments were performed as a series of competition experiments using a 10 M excess of both p-$ClC_6H_4CON(Me)O^-$ (*p*-ClNMBH; pK_a = 12.04 in MeOH[7a]) and 3-$NO_2C_6H_4O^-Na^+$ (pK_a = 12.44 in MeOH[8]) in a thermostated water bath at 29.5 °C in reaction with a 1.0 M amount of the sulfonium salts. These salts were prepared as reported.[3] The reactions were allowed to stand for 1 h and were then analyzed using a Hewlett-Packard 5890 GCMS employing a 12 ft cross-linked methyl silicone gum column. Authentic materials identified the retention times and gave authentic mass spectra for comparison of products. The areas were digitally integrated. Each determination was carried out in, at least, duplicate. The GCMS has been shown previously to be nearly linear in relating areas to grams.[7a] The ratios of the areas were then multiplied by the ratios of the molecular weights to give the α-effects as $k_{\alpha-\mathrm{nuc}}/k_{\mathrm{nuc}}$.

The α-effects are summarized in Table 1.

Computational chemistry for the methyl cation affinities was performed on a Gateway P166 using either Hyperchem 4.5 or 5.0. Geometries were obtained at the PM3 and 3-21G* levels of theory. Computation of all the vibrational spectra showed all positive frequencies and, hence, energy minima for all structures. Computations at the ab initio 3-21G* level were performed with Gaussian 94 on an SGI *Indy* or G94W on the Gateway P166. The methyl radical affinities were defined analogously to the methyl cation affinities as in reaction 3 and are at the PM3 (UHF) level of theory. The issue of local vs global minima was settled by rotating the SMe_2 group around the aryl−S bond in various possible conformations until the lowest energy was obtained; in all cases, this conformation was one in which at least one $S-CH_3$ bond was nearly perpendicular to the plane of the aryl ring.

Results

The methyl cation affinities (MCA)[13] and methyl radical affinities (MRA) were computed from the ΔH_f predicted by the quantum calculations using the ΔH for the dilute gas-phase reaction (eq 3).[13] The results are summarized in Table 2.

$$BMe^+ \rightleftharpoons B + Me^+ \qquad (3)$$

Table 2. MCA (kcal/mol) and MRA Values for the Aryl Methyl Thioethers

		PhSMe	1-naphthylSMe	9-anthracenylSMe
MCA	PM3	−99.11	−99.5	−103.7
	3-21G*	−53.3	−111.1	−78.44
MRA		−18.12	−20.77	−31.84

Discussion

The sizes of the α-effects in Table 1 follow the order of the ability of the aryldimethylsulfonium salts to accept an electron, as demonstrated earlier by Savéant[4] et. al. The α-effect with the phenyldimethylsulfonium salt is very similar to the α-effect reported by us, determined by direct kinetic studies.[9] In all these cases, in Savéant's study, the capture of a single electron from an electrode was part of an EC process. In an EC process the rate-limiting step is a first-order chemical step ("C") following a fast electron-transfer step ("E"). From theoretical and experimental electrochemical criteria it was possible for Savéant to evaluate the degree of concertedness of these two processes. The rates of the two process in eq 1 approach each other as the aryl system becomes smaller. The aryl = phenyl was most concerted case, followed by the 1-naphthyl case and then the 9-anthracenyl case. All of the cases deal with EC mechanisms, but with varying degrees of mixture of the E and C processes. The single electron is known to enter an S−C σ^* orbital and not the π^* system of the aryl ring.[4,14]

The correlation of the sizes of the α-effects in the table with the order of ease of the E process and, inversely, with the degree of concerted EC reactivity in the series indicates the following: 1. The α-effect in methyl transfer involves SET character in the transition state. 2. The degree of concertedness of an EC process controls the size of the α-effect in S_N2 reactions.

We have previously discussed the α-effect at carbon atoms as involving an intrinsic effect, shown at the most simple carbon atom in CH_3 groups.[7a] This effect is modified by substitutions of other atoms or groups on the C atom undergoing nucleophilic attack, such as phenyl (giving a benzyl), or =O, giving the C=O group. These groups give larger α-effects than at methyl due to their ability to disperse the extra charge.[7a] This argument is similar to the one Savéant advanced in explaining the increased ability of the 9-anthracenyl salts to stabilize SET character in the sulfonium salts. The extra charge is dispersed into the more extensive π system in those systems. The present results with the *N*-methylbenzohydroxamate transition states are entirely consistent with that idea.

We have previously reported that the α-effect in the substituted phenyldimethylsulfonium series is most probably electronic in origin.[9] The application of the tool of increasing electron demand in a series of ring substituted *N*-methylbenzohydroxamate anions gave a Brönsted-type plot that intersected the plot of the substituted phenolate anions (non-α-nucleophiles). The present correlation of the size of the α-effect with increasing ease of SET reception combined with the behavior these sulfonium

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salts on increasing electron demand in the nucleophiles indicates that the α-effect, in this system at least, is an intrinsic electronic one, and it involves some SET behavior as well.

These conclusions support the Shaik[1] idea of inclusion of some SET character into the transition-state wave function of even an S_N2 methyl group transfer. The finding of correlation of the increasing size of the α-effect with increasing ease of acceptance of SET character supports the Hoz model of inclusion of some three-electron splitting character into the TS wave function, even in methyl group transfers. Previously the Hoz model was meant only to refer to the α-effects at groups such as $>C{=}O$.[10]

Possible alternative explanations for our observations deserve mention here. A reviewer has suggested that when the reaction is placed on a More O'Farrall-Jencks diagram a reasonable deduction is that the α-effect has nothing to do with the electronic nature of the nucleophile but reflects an increase in the bond formation between the C atom and the nucleophile at the transition state. The transition state changes in the direction of increased bond function, as suggested by Dixon and Bruice.[11] Jencks has also recently pointed to a possible thermodynamic origin for the α-effect in nucleophilic attack at phosphorus.[12] Attacking these alternatives is not an easy prospect. We offer the following approach.

The expulsion of a methyl group, either as a cation or a radical, should reflect the ability of the S atoms in the series of compounds to hold on to these two kinds of methyl groups. This ability should be reflected in the methyl cation affinities of the series of methyl aryl thioethers or in the (analogously defined) methyl radical affinities. The methyl aryl thioether best able to receive a methyl cation or a methyl radical should be the worst at giving it up to a nucleophile if the thermodynamic argument holds. We computed the methyl cation affinities at two different levels of theory (PM3 and 3-21G*) for the series phenyl, naphthyl, and 9-anthracenyl methyl thio ethers. The results are summarized in Table 2, and they demonstrate that, at least at these levels of theories, the trends for these parameters do not correlate the experimental data. The size of the α-effect increases regularly in the order the phenyl < naphthyl < 9-anthracenyl. Admittedly, the 3-21G* MCA values predict the 9-anthracenyl should give a larger effect than the 1-naphthyl, but it should give a much smaller α-effect than the phenyl case if the thermodynamic argument holds. The MRA affinities are in the completely reverse order, predicting that the 9-anthracenyl case would be worst at transferring a methyl radical. These data indicate that our conclusions that substantial SET character is involved in the α-effect are at least sound at these levels of theory.

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