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Regioselectivity in the Reductive Bond Cleavage of Diarylalkylsulfonium Salts: Variation with Driving Force and Structure of Sulfuranyl Radical Intermediates

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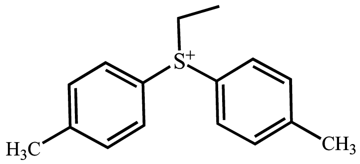
Abstract: This investigation was stimulated by reports that one-electron reductions of monoaryldialkylsulfonium salts never give aryl bond cleavage whereas reductions of diarylmonoalkylsulfonium salts preferentially give aryl bond cleavage. We studied the product ratios from the reductive cleavage of di-4-tolylethylsulfonium and di-4-tolyl-2-phenylethylsulfonium salts by a variety of one-electron reducing agents ranging in potential from -0.77 to $+2.5$ eV (vs SCE) and including thermal reductants, indirect electrolyses mediated by a series of cyanoaromatics, and excited singlet states. We report that the cleavage products vary from regiospecific alkyl cleavage to predominant aryl cleavage as a function of the potential of the reducing agent. We conclude that differences between the reductive cleavages of mono- and diarylsulfonium salts are direct consequences of the structures of the sulfuranyl radical intermediates and the bond dissociation energies of the alkyl and aryl bonds. Competitions between the rates of cleavage and oxidation of the intermediate sulfuranyl radicals and between concerted and stepwise mechanisms are discussed to explain the variations in bond cleavage products as a function of the driving forces for the reductions. Density functional theory investigations of the nature of the antibonding S−alkyl and S−aryl orbitals of the starting sulfonium salts provide additional insight.

Introduction

We have been intrigued by a puzzle first identified by Hall and Horner[1] and confirmed by Beak and Sullivan.[2] One-electron reduction of phenyldialkylsulfonium salts gives cleavage of the weaker S−alkyl bonds in the approximate order of the stability of the resulting radicals (primary < secondary < benzyl); the phenyl group is not cleaved.[2,3] In contrast, the stronger S−aryl bond is preferentially cleaved in one-electron reduction of diphenylmethylsulfonium salts.[1,2,4] This paradox implies that the reductions proceed by way of 9−S−3 sulfuranyl radical intermediates whose properties (e.g., relative rates of C−S bond cleavages) vary with structure. We now report that the ratio of aryl to alkyl bond cleavage in some diarylalkylsulfonium salts is a function of the potential of the reductant.

Results

We studied the reductive cleavages of di-4-tolylethylsulfonium hexafluorophosphate (**1**-PF_6):



1

The ethyl group is important for suppressing the rate of competing nucleophilic displacements that occur at the methyl group in diarylmethylsulfonium salts.[5] A variety of excited- and ground-state reductants are effective in the cleavage reaction, which is shown in eq 1:

$$\mathbf{1} \xrightarrow{e^-} 4\text{-}CH_3C_6H_4SC_2H_5 + (4\text{-}CH_3C_6H_4)_2S \tag{1}$$

Both tolyl and ethyl cleavage products from **1**-PF_6 are observed, with the tolyl cleavage product favored by a factor of 2−3. The data are expressed in terms of **F**, the ratio of tolyl cleavage product to ethyl cleavage product:

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(5) For example, the cleavage ratios reported by Hall and Horner[1] are compromised by nucleophilic displacement because they used methylsulfonium salts and tetrabutylammonium bromide as the supporting electrolyte in acetonitrile. As the temperature was increased in their electrolytic experiments, the amount of methyl cleavage increased, as expected for a competing S_N2 reaction.

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$$\mathbf{F} = \frac{[4\text{-}CH_3C_6H_4SC_2H_5]}{[(4\text{-}CH_3C_6H_4)_2S]}$$

The results are reported in Table 1.

Sulfonium salt **1**-PF_6 is photocleaved by direct irradiation at 300 nm. This direct photolysis favors ethyl cleavage (**F** = 0.36), in contrast to the reductive cleavages (**F** ≈ 2−3) reported in Table 1. The peak reduction potential of **1**-PF_6 is $E_p = -1.7$ V versus SCE in dimethylformamide (DMF) at a scan rate of 100 mV/s; the sensitizers and experimental conditions in expts 1−4 were chosen to ensure that electron transfer would be exothermic and direct photolysis or energy transfer would be unfavorable. One specific photosensitized reduction was studied in detail; the fluorescence of 9-phenylanthracene (PA) and the total quantum yield for the formation of sulfides in acetonitrile varies as a function of [**1**-PF_6]. Stern−Volmer analyses give linear correlations and comparable values for the bimolecular rate constant for quenching (3×10^9 M^{-1} s^{-1}) and product formation (8×10^9 M^{-1} s^{-1}). The limiting quantum yield is 0.5.[14,15] Thermal reactions are also effective, as reported in expts 4−8. The reaction of triphenylphosphine with **1**-PF_6 (expts 5 and 6) is a free-radical chain reaction involving ground-state phosphoranyl radicals as the reductant.[16] When the chain was initiated by irradiation at 300 nm (expt 5), a 1:1 correspondence between the yields of 4-tolylethyl sulfide and 4-tolyltriphenylphosphonium ion was observed, providing quantitative evidence of cleavage to give 4-tolyl radicals.

The data in Table 1 show that **F** is approximately independent of the nature of the reductant. The interpretation of these results seemed straightforward: the reductions give a common sulfuranyl radical intermediate, and the product ratio is a property of that intermediate that is determined by k_{Ar}/k_R, the ratio of rate constants for the unimolecular fragmentation of the sulfuranyl radical to give tolylethyl sulfide and ditolyl sulfide, respectively. We were quite surprised, therefore, to discover other one-electron reducing agents that give very different results: both cobaltocene[17] ($E° = -1.04$ V vs SCE in acetonitrile) and Kosower's 1-ethyl-4-(methoxycarbonyl)pyridinyl radical[18] ($E° = -0.82$ V vs SCE in acetontrile) reduce **1**-PF_6 to give only ethyl cleavage (**F** < 0.04).

Table 1. Reductive Cleavage of **1**-PF_6[a]

expt	reductant	**F**[b]	$-\Delta G_{ET}$ (eV)[c]
1	^{1}anthracene[d]	2.8 (2.5)	~0.4
2	^{1}PA[d]	2.8 (2.7)	~0.6
3	^{1}DMA[e]	2.8 (3.3)	~0.9
4	$(CD_3)_2CO^{\bullet-}$[f]	2.7 (2.3)	~0.7
5	Na(Hg)[g]	2.8	0.6
6	$K(C)_8$[h]	(~1)	−
7	4-tolyltriphenylphosphoranyl radical[i]	2.1 (2.5)	~0.1
8	4-tolyltriphenylphosphoranyl radical[j]	3.1 (4.0)	~0.1

[a] In a typical experiment, [**1**] = 0.03 M in acetone-d_6 at rt; [sensitizer] = 0.045−0.060 M in expts 1−4. [b] Determined by NMR integration; values in parentheses were determined by gas chromatography. [c] For expts 1−3, $\Delta G_{ET} = (E_{ox} - E_{red}) - E^*$.[6] Values are approximate because the pertinent data are in different solvents. [d] For anthracene[7] and 9-phenylanthracene (PA),[8] $\lambda_{ex} = 300$ nm. [e] For 1,4-dimethoxyanthracene (DMA),[9] $\lambda_{ex} = 385$ nm. [f] $(4\text{-Tolyl})_3N$ was the sensitizer, with $\lambda_{ex} = 300$ nm; acetone radical anion was the reductant.[10] [g] In acetonitrile.[11] [h] See refs 2 and 12. [i] Initiated by the photolysis of phenylazoisobutyronitrile (PAIBN) at 385 nm, with [PAIBN] = 0.01 M and [Ph_3P] = 0.24 M. [j] Initiated by photolysis at 300 nm, with [Ph_3P] = 0.12 M; 4-tolyltriphenylphosphoranyl radical was the reducing agent.[13]

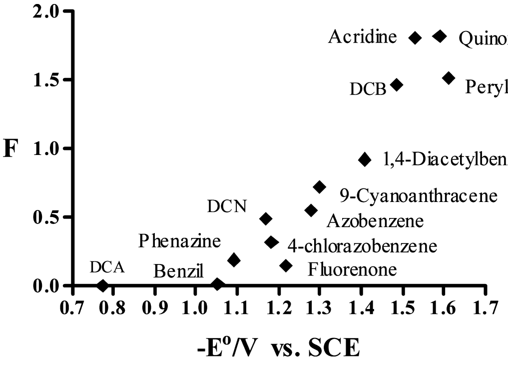

Figure 1. Sulfide ratio **F** for the indirect electrolysis of **1**-BF_4 in DMF by mediators of varying potential (DCA = 9,10-dicyanoanthracene; DCN = 1,4-dicyanonaphthalene; DCB = 1,4-dicyanobenzene).

We followed up on our initial observations using cobaltocene and Kosower's radical with a series of indirect electrochemical reductions of **1**-BF_4 in which the potential of the mediating reductant was systematically varied. The results for the indirect electrolyses of **1**-BF_4 are shown in Figure 1. Although there is considerable scatter in the data, the unmistakable observation is that the ratio of cleavage products, **F**, is not constant; rather, the ratio increases with the reducing potential of the reductant over the range −0.77 to −1.61 V (vs SCE). At the lowest potentials [9,10-dicyanoanthracene (DCA) and benzil], only ditolyl sulfide was observed, corresponding to exclusive ethyl cleavage and the reductions by cobaltocene and the pyridinyl radical. At the highest potentials (perylene and quinoxaline), tolyl cleavage to give tolylethyl sulfide predominates, reminiscent of the data in Table 1.

The electrochemical reduction of **1**-BF_4 mediated by 1,4-dicyanonaphthalene (DCN; $E° = -1.17$ V vs SCE) in DMF was studied in detail. The concentration of sulfonium salt could be followed by capilliary electrophoresis; quantitative analysis showed a 1:1 correspondence of sulfonium salt consumed to sulfides formed. As reported in Table 2, expts 1−5, **F** is 0.47 ± 0.04 ($n = 5$); that is, both tolyl and ethyl cleavage were observed, with ethyl cleavage predominating by a factor of 2. Coulometry gave $n \approx 1$ for the number of electrons required to consume one molecule of sulfonium salt.

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Table 2. Product Yields from Indirect Electrolysis of **1**-BF_4 in DMF Mediated by DCN

	% yield[a]			
expt	TolH	TolSEt	Tol_2S	**F**[b]
1	18	26	50	0.51
2	16	23	45	0.51
3	18	24	53	0.45
4	17	22	50	0.45
5[c]	19	32	76	0.43
6[d]	13	28	80	0.35
7[e]	5	24	47	0.51

[a] Based on complete electrolysis of **1**-BF_4. [b] **F** = [TolSEt]/[Tol_2S]. [c] Ethylcyanonaphthalenes were observed (8% yield based on **1**-BF_4). [d] Acetic acid was added to the electrolysis medium. [e] Acetonitrile solvent.

Approximately 70% of the putative tolyl fragments (as judged by the yield of TolSEt) were recovered as toluene. Ethylcyanonaphthalenes, the coupling products of the radical anion of DCN and ethyl radical[19] were observed, albeit in yields insufficient to account for the mediator consumed or the putative ethyl fragments (19%, as judged by the yield of Tol_2S). The value of **F** was not significantly affected by the addition of acetic acid to the reduction medium (Table 2, expt 6) or changing the solvent from DMF to acetonitrile (Table 2, expt 7).

In general, these results can be rationalized in terms of reduction of DCN to give the radical anion (eq 2) followed by reduction of the sulfonium salt by $DCN^{\bullet-}$ to give the observed sulfides and the corresponding tolyl and ethyl radicals (eqs 3 and 4):

$$DCN + e^- \rightarrow DCN^{\bullet-} \qquad (2)$$

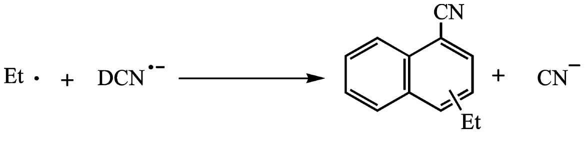
$$Tol_2S^+Et + DCN^{\bullet-} \rightarrow TolSEt + Tol\bullet + DCN \qquad (3)$$

$$Tol_2S^+Et + DCN^{\bullet-} \rightarrow Tol_2S + Et\bullet + DCN \qquad (4)$$

The radicals are subsequently consumed in a complex variety of ways. On the basis of previous studies of mediated reductions of aryl and alkyl halides,[20] we anticipated that the tolyl radical might be reduced to tolyl anion (eq 5), which might then react with the sulfonium salt (eq 6). In contrast, we expected the alkyl radical to be scavenged by the radical anion of DCN to give coupling products (eq 7):

$$Tol\bullet + DCN^{\bullet-} \rightarrow Tol^- + DCN \qquad (5)$$

$$Tol^- + Tol_2S^+Et \rightarrow TolH + Tol_2S + CH_2{=}CH_2 \qquad (6)$$



(7)

The formation of toluene and ethylcyanonaphthalenes provide evidence for the formation of tolyl and ethyl radicals, respectively (eqs 3 and 4). Although toluene accounts for ~70% of the tolyl fragments, it is not clear whether tolyl radical or tolyl anion is the immediate precursor to the toluene. The low yield of the coupling product of ethyl radical and $DCN^{\bullet-}$ is consistent with the observed value $n \approx 1$, since eq 7 consumes electrons ($DCN^{\bullet-}$) but not sulfonium salt. Clearly, ethyl groups are disappearing by other, unidentified, pathway(s).

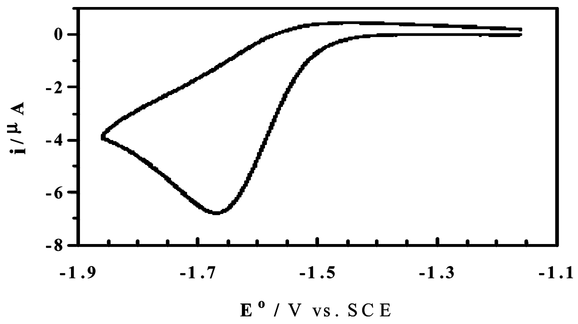


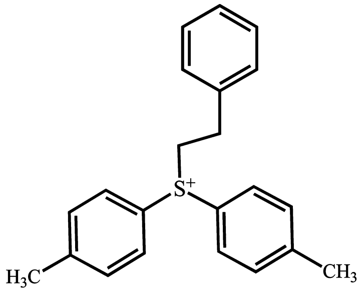
Figure 2. Cyclic voltammogram for the reduction of **2**-BF_4 in DMF at a scan rate of 100 mV/s.

Table 3. Products from Indirect Electrolysis of **2**-BF_4 in DMF Mediated by DCN[a]

% reduction[b]	[styrene] (mM)	[Tol_2S] (mM)	[TolSR] (mM)	**F**[c]	$\mathbf{F}_{corr}$[d]
14	0.00	0.31	0.18	0.58	0.58
28	0.29	1.00	0.39	0.39	0.55
43	0.36	1.89	0.61	0.33	0.40
57	0.41	2.08	0.81	0.39	0.48
71	0.47	2.47	1.03	0.42	0.51
100	0.61	2.89	1.19	0.41	0.52

[a] The initial concentrations of **2**-BF_4 and DCN were 4.26 mM. [b] % reduction = 100[(mmol of electrons)/(initial mmol of **2**-BF_4)]. [c] **F** = [TolSR]/[Tol_2S]; R = 2-phenylethyl. [d] $\mathbf{F}_{corr}$ = [TolSR]/([Tol_2S] − [styrene]).

The possibility that Tol_2S might be formed by an elimination reaction (eq 6) in the electrochemical reductions would confound the **F** values reported in Figure 1 and Table 2 and our understanding of the reductive cleavage of **1**-BF_4. Accordingly, we prepared and studied the indirect electrolysis of di-4-tolyl-2-phenylethylsulfonium fluoroborate (**2**-BF_4). Our purpose was to reveal the elimination reaction and facilitate the measurement of the resulting alkene.



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The E_p (−1.67 V vs SCE) and $E_{1/2}$ (−1.60 V vs SCE) potentials of **2**-BF_4 in DMF were obtained by cyclic voltammetry, as shown in Figure 2. In the indirect reduction experiments, sulfonium salt and mediator were present in approximately equal concentrations, and the potential was set at a value 100 mV more cathodic than the reduction potential of the mediator.

In fact, the mediated reduction of **2**-BF_4 by $DCN^{\bullet-}$ in DMF gives easily measured yields of styrene, the expected elimination product (Table 3). The yield of Tol_2S was corrected for the elimination reaction ([Tol_2S] − [styrene]) to give $\mathbf{F}_{corr} = 0.51$

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Table 4. Products from Indirect Electrolysis of **2**-BF_4 in Acetonitrile Mediated by DCN

% reduction[a]	[DCN] (mM)	[styrene] (mM)	[Tol_2S] (mM)	[TolSR] (mM)[b]	F[b]	F_{corr}[c]
0	3.82	0.00	0.00	0.00		
17	3.87	0.00	0.25	0.16	0.65	–
33	3.60	0.05	0.66	0.34	0.52	0.56
49	3.48	0.10	1.03	0.49	0.48	0.53
66	3.17	0.18	1.37	0.68	0.49	0.57
83	2.99	0.31	1.83	0.86	0.47	0.57
98	2.85	0.46	2.27	1.05	0.46	0.58

[a] % reduction =100[(mmol of electrons)/(mmol of **2**-BF_4)] [b] **F** = [TolSR]/[Tol2S]; R = 2-phenylethyl. [c] $\mathbf{F}_{corr}$ = [TolSR]/([Tol_2S] − [styrene]).

Table 5. Cleavage Product Ratios for the Indirect Electrolyses of **2**-BF_4 in DMF Mediated by Cyanoaromatic Reductants[a]

mediator	$E°$ (V vs SCE)	F[b]		F_{corr}[c]	
		GC–MS	HPLC	GC–MS	HPLC
9,10-dicyanoanthracene	−0.77	–[d]	–[d]	0	0
1,4-dicyanonaphthalene	−1.17	0.25	0.42 ± 0.03 (6)	0.29	0.52
9-cyanoanthracene	−1.30	0.61	0.85 ± 0.22 (6)	0.71	0.99
1,4-dicyanobenzene	−1.49	1.13	0.94	1.54	1.38
9-cyanophenanthrene	−1.50	0.86	1.03	1.30	1.68
1-cyanonaphthalene	−1.77	0.87	0.89	1.65	1.66

[a] Electrolysis was carried to completion; products were measured at intervals throughout the electrolysis, as in Tables 3 and 4. [b] **F** = [TolSR]/[Tol_2S]; R = 2-phenylethyl. [c] $\mathbf{F}_{corr}$ = [TolSR]/([Tol_2S] − [styrene]). [d] 2-Phenylethyl-4-tolyl sulfide was not detected.

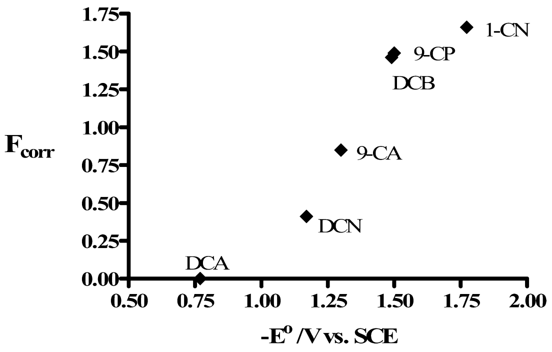

Figure 3. Average values of corrected product ratios $\mathbf{F}_{corr}$ for the indirect electrolyses of **2**-BF_4 in DMF as a function of mediator potential.

Table 6. Cleavage Product Ratios for the Indirect Electrolyses of **2**-BF_4 in Acetonitrile Mediated by Cyanoaromatic Reductants

mediator	$E°$ (V vs SCE)	F[a]	F_{corr}[b]
9,10-dicyanoanthracene	−0.77	–[c]	0
1,4-dicyanonaphtalene	−1.17	0.48	0.56 ± 0.02
9-cyanoanthracene	−1.30	0.58	0.68
1,4-dicyanobenzene	−1.49	0.72	1.02

[a] **F** = [TolSR]/ [Tol_2S]; R = 2-phenylethyl. [b] $\mathbf{F}_{corr}$ = [TolSR]/([Tol_2S] − [styrene]). [c] 2-Phenylethyl-4-tolyl sulfide was not detected.

± 0.6 (*n* = 6). The uncorrected values in Table 2 (**F** = 0.47 ± 0.04) and the corrected values in Table 3 ($\mathbf{F}_{corr}$ = 0.51 ± 0.06) are in reasonable agreement, showing that the results in Table 2 for the ditolyethylsulfonium salt (**1-BF$_4$**) are not significantly biased by an elimination reaction.

In addition to toluene, styrene, and the sulfides, the GC–MS and HPLC traces showed two 2-phenylethylcyanonaphthalenes assigned to coupling reactions of $DCN^{\bullet -}$ and 2-phenylethyl radicals. Together, the two coupling products were formed in 27% yield, referenced to the corrected yield of ethyl fragments ([Tol_2S] − [styrene]). Finally, trace amounts (~3.5% yield based on sulfonium salt consumed) of 1-cyano-2-phenylethane were observed. Ethylbenzene was not detected.

The reduction of **2**-BF_4 by $DCN^{\bullet -}$ in acetonitrile was also studied (Table 4). The corrected sulfide ratio, $\mathbf{F}_{corr}$ = 0.56 ± 0.02 (*n* = 5), is in agreement with the results in DMF, showing that the reductive cleavage of the sulfonium salt is unaffected by solvent. In contrast, the solvent did affect the subsequent postcleavage reactions. The styrene yield is significantly less (5–18%) in acetonitrile than in DMF (20–45%). Similar observations are reported in Table 2 for the reduction of **1**-BF_4; although the yield of toluene is significantly less in acetonitrile than in DMF, the cleavage ratio **F** is unaffected.

Table 5 summarizes values of $\mathbf{F}_{corr}$ for the reductive cleavages of sulfonium salt **2**-BF_4 in DMF by a family of cyanoaromatic mediators covering a range of reduction potentials from −0.77 to −1.77 V vs SCE. The data were obtained by two different experimental analytical techniques (GC–MS and HPLC); average values of $\mathbf{F}_{corr}$ are plotted in Figure 3. Table 6 gives comparable results for the indirect reduction of **2**-BF_4 by selected cyanoaromatic mediators in acetonitrile.

Discussion

The paradoxical preference for breaking the stronger S–aryl bond in the reduction of diarylalkylsulfonium salts (Table 1) and the variation of the ratio of aryl to alkyl cleavage as a function of the potential of the reducing agent (Tables 5 and 6 and Figure 3) require sulfuranyl radical intermediates in the pathways to cleavage products. In fact, fast-scan cyclic voltammetry investigations by Savéant[21] gave direct evidence for an intermediate in the reductive cleavage of 9-anthryldimethylsulfonium cation (eq 8):

$$\text{anthrylS}^{+}\text{Me}_2 + e^{-} \rightarrow [\text{anthrylSMe}_2]^{\bullet} \rightarrow \text{anthrylSMe} + \text{Me}\bullet \tag{8}$$

At low scan rates, the cyclic voltammogram showed only the reduction wave. However, at scan rates of 12 500 V/s and above, an oxidation wave was detected, revealing the reversibility of the electron transfer and the presence of a short-lived intermediate.[21] Sulfuranyl radicals have also been proposed as intermediates in the displacement reactions of radicals with sulfides[22] (eq 9)

$$R'\bullet + R_2S \rightarrow [R_2SR']^{\bullet} \rightarrow R\bullet + RSR' \tag{9}$$

and in a variety of other reactions.[23,24] Similarly, a variety of sulfuranyl radical structures have been proposed, some derived from direct observation, some deduced from experimental observations, and still others based on computational methods.[25]

For arylsulfonium salts with electron-delocalizing substituents on the aryl ring, there is good evidence for a sufuranyl structure

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(24) In one case, an intermediate sulfuranyl radical was captured by oxidation to give the corresponding sulfonium salt. See: Leanardi, P.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Chem. Commun.* **1985**, 1390–1391.

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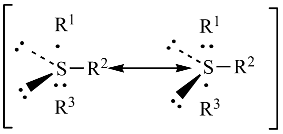
in which a π-aryl radical anion is substituted with a sulfonium group.[26] There is, however, no direct evidence for this type of structure when the aryl group is a simple phenyl. Most of the proposed structures for sulfuranyl radicals involve reorganization of the σ bonding of the starting sulfonium cation.[23] The simplest of these structures is a pyramidal σ^* species with a two-center−three-electron (2c−3e) bond to sulfur; dialkylalkoxysulfuranyls and dialkylthioalkylsulfuranyls are assigned to this category on the basis of electron spin resonance (ESR) evidence. On the other hand, the most common structures invoke three-center−four-electron (3c−4e) or three-center−three-electron (3c−3e) bonding.[27]

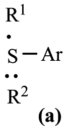
A consequence of the three-center bonding is a structural change from a pyramidal sulfonium ion to a planar (quasi-T-shaped) sulfuranyl radical (**3**):



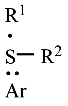
3

The salient feature of this structure is that the apical three-center bonds are different from the equatorial two-center-two-electron (2c−2e) bond; ESR observations and computational methods support this conclusion.[23] More specifically, the 3c−3e structure predicts that the apical bonds are the locus of bond making and breaking in sulfuranyl radicals. From a reaction-chemistry perspective, the 3c−3e description of sulfuranyl radicals is especially appealing. For example, the reactions of radicals with sulfides have been shown to prefer a linear arrangement of the sulfur atom and the entering (bond-making) and leaving (bond-breaking) groups.[28,29] The 3c−3e structure of **3** clearly describes these experimental observations.

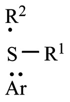
Most interestingly, the distinction between apical and equatorial bonds in three-center structures leads immediately to isomeric sulfuranyl radicals. For example, there are three possible T-shaped structures for the sulfuranyl radicals derived from aryldialkyl- sulfonium salts:



(a)



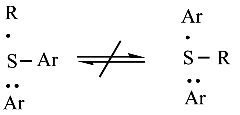
(b)



(c)

The structures **a**, **b**, and **c** clearly accommodate the experimental result that the stronger S−aryl bond is never cleaved in the reduction of aryldialkylsulfonium salts, since there is always an alkyl group in the 3c−3e bonding system and therefore a path for cleaving one of the weaker S−alkyl bonds.[30] For structure **a**, the ratio of products $[R^1\cdot]/[R^2\cdot]$ equals k_{R^1}/k_{R^2}, the ratio of the rate constants for cleavage of the apical bonds, and is determined in part by the relative stability of the radicals $R^1\cdot$ and $R^2\cdot$. In structures **b** and **c**, alkyl cleavage is faster than aryl cleavage, and the net result is that the ratio of products $[R^1\cdot]/[R^2\cdot]$ is determined by the ratio of the populations, [**b**]/[**c**].[31]

The three-center bonding description of sulfuranyl radical intermediates resolves the paradox posed by aryl cleavage in diarylalkyl sulfonium salts. The pertinent structures are **j** and **k**:



(j) **(k)**

Structure **j** obviously fragments to give an alkyl radical in preference to an aryl radical.[32] However, structure **k** is unique and can only fragment to give an aryl radical.[33] A further implication of this interpretation is that the fragmentation of these sulfuranyl radicals is faster than their permutational isomerization, $\mathbf{j} \rightleftarrows \mathbf{k}$. Were the converse true, the equilibrating radicals would leak out of the low-energy transition state to give only alkyl cleavage, contrary to observations. The same conclusion was suggested previously on the basis of studies of free-radical displacement reactions at sulfur.[28,34]

How then can we understand the different product ratios from diarylalkylsulfonium salts **1**-PF_6 and **2**-BF_4 with different reducing agents, as reported in Tables 1, 5, and 6 and Figures 1 and 3? There are three distinct experimental regimes. Regime I is characterized by strongly exothermic electron transfers ($\Delta G_{ET} \approx -0.4$ to -0.9 eV) and product ratios that are approximately constant and favor aryl cleavage (**F** ≈ 2−3). This regime includes both excited- and ground-state reductants (Table 1). In stark contrast, regime III is characterized by strongly endothermic electron transfers ($\Delta G_{ET} \approx +0.7$ to $+0.9$ eV) and exclusive alkyl cleavage (**F** ≈ 0). This regime includes cobaltocene, Kosower's pyridinyl radical, and $DCA^{\bullet-}$ as reducing agents. In regime II, the **F** increases from 0.3 to 1.7 as the endothermicities of the mediated electron transfers decrease from approximately +0.5 eV to zero (Tables 5 and 6 and Figure 3). The phosphoranyl radical chain reductions (Table 1, expts 7 and 8) also belong to regime II.

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(26) Ghanimi, A.; Simonet, J. *New J. Chem.* **1997**, *21*, 257–265.

(27) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Laegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753–7759.

(28) Kampmeier, J. A.; Jordan, R. B.; Liu, M. S.; Yamanaka, H.; Bishop, D. J. *ACS Symp. Ser.* **1978**, *69*, 275–289.

(29) Cooper, J. W.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1977**, 228–230.

(30) DFT calculations indicated that the reduction of phenyldiethylsulfonium ion to ethyl radical and phenylethylsulfide is thermodynamically favored by 13 kcal/mol over the alternative reduction to phenyl radical and diethylsulfide.

(31) The structures of **b** and **c** clearly predict that cleavage ratios derived from different sulfonium salts will not commute.[2] Because the ratio of populations of **b** and **c** varies with the structure of the sulfonium salts, the apparent cleavage ratio is a composite of the direct competition k_{R^1}/k_{R^2} and the population ratio [**b**]/[**c**]. This "population effect" is also seen quite clearly in the reduction of *cis*- and *trans*-1-phenyl-2-methyltetrahydrothiophenium salts.[2] Because of the ring, there is no sulfuranyl radical structure in which primary and secondary alkyl groups simultaneously occupy apical positions and compete directly. Furthermore, there is no reason for the population ratio **b**/**c** to be constant for the cis and trans isomers or to relate to the primary/secondary cleavage ratio observed when acyclic phenyldialkylsulfonium salts are reduced.

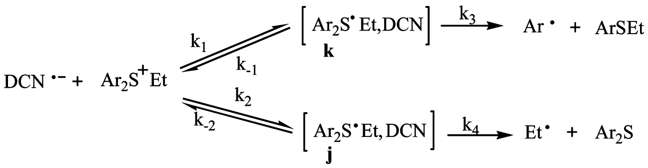
(32) DFT calculations for **1** and **2** indicated that the reduction to give 4-tolyl radical rather than the corresponding alkyl radical is thermodynamically disfavored by 11.3 and 10.5 kcal/mol, respectively.

(33) The distinction between aryldialkyl and diarylalkylsulfonium salts is preserved in the reduction of cyclic sulfonium salts.[2] The reduction of 1-phenyltetrahydrothiophenium cation gives only ring-opened product; phenyl cleavage is not observed. In contrast, the reduction of the benzofused system, 1-phenylthiaindan hexafluorophosphate, gives ~15% aryl cleavage. The 1-phenylthiaindan cation is reduced to give a mixture of two nonequilibrating sulfuranyl radicals, one of which must give phenyl cleavage.

(34) Tada, M.; Nakagini, H. *Tetrahedron. Lett.* **1992**, *33*, 6657–6660.

The weaker S−alkyl bond is the one that breaks in an unconstrained competition between aryl and alkyl cleavage in a sulfuranyl radical intermediate, as observed in the reductive cleavage of phenyldialkylsulfonium ions.[30] The paradoxical preference for aryl cleavage in the reduction of diarylalkylsulfonium ions implies a sulfuranyl radical that can give only aryl cleavage (**k**). However, alkyl cleavage is also observed, requiring a second intermediate that preferentially gives alkyl cleavage (**j**). One interpretation of the observed values of **F** in the *thermal* reactions involves competitive rates of formation and reaction of these two intermediates, as shown in Scheme 1.

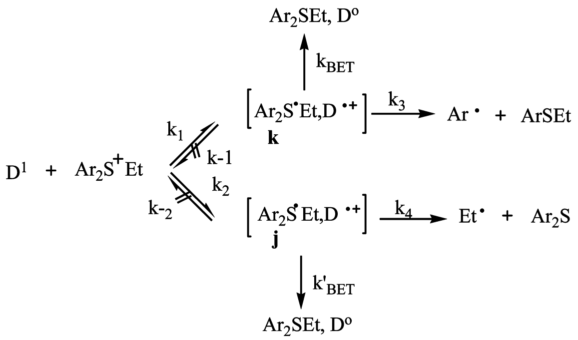
Scheme 1



The kinetic scheme in Scheme 1 proposes that sulfuranyl intermediates **k** and **j** are the products of the forward electron transfer and are populated in the ratio k_1/k_2. When the forward electron transfer is significantly exothermic (regime I; Table 1, expts 4−6), the rapid product-forming steps (with rate constants k_3 and k_4) will be faster than the endothermic return electron transfer reactions, and the cleavage ratio will be approximated by the population ratio: $\mathbf{F} \approx k_1/k_2$.[35] On the other hand, when the forward electron transfers are significantly endothermic (regime III), the exothermic back reactions will be faster than cleavage and provide an indirect mechanism for equilibrating **j** and **k**. In the limit $k_{-1} \gg k_3$ and $k_{-2} \gg k_4$, the product ratio will be determined by the difference in the free energies of the transition states for the aryl and alkyl cleavages. In this situation, alkyl cleavage will predominate, as observed for the weak reductants cobaltocene, pyridinyl radical, and $\mathrm{DCA}^{\bullet-}$. Between these two limiting regimes I and III, all six rate constants matter (regime II), and **F** will vary with the structures and potentials of the reductants,[35] as observed in Figures 1 and 3.

Although the preceding analysis of Scheme 1 is consistent with the results of the thermal reactions, the kinetic analysis should also accommodate the photochemical results. As shown in Scheme 2 for the *photochemical* reactions, the competitions for the intermediates are now between the rapid product-forming steps (k_3 and k_4) and the exothermic back electron transfers to the ground state (k_{BET} and k'_{BET}). For expts 1−3 in Table 1, the return to the ground state is exothermic by 2−3 eV. Nevertheless, products are formed, indicating that the rates of back electron transfer and product formation must be roughly comparable for the photochemical reactions ($k_{\mathrm{BET}} \approx k_3$ and $k'_{\mathrm{BET}} \approx k_4$). In contrast, the return electron transfer reactions in regime III are exothermic by only 0.7−0.9 eV. Even so, the kinetic analysis (Scheme 1) for the *thermal* reactions of poor reducing agents such as $\mathrm{DCA}^{\bullet-}$, cobaltocene, and Kosower's radical requires that the rates of return electron transfer are much higher than the rates of product formation ($k_{-1} \gg k_3$ and $k_{-2} \gg k_4$). Since the rates of product formation should be approximately constant, the driving-force differences suggest that the back electron transfers in the photochemical reactions should be faster than the return electron transfers in the thermal reactions, in disagreement with the kinetic proposal. This apparent contradiction is resolved by Marcus inverted region behavior, which can significantly decrease the rates for strongly exothermic return to the ground state in the photochemical reactions.[36] Consequently, the kinetic analyses in Schemes 1 and 2 qualitatively accommodate the full range of photochemical and thermal reactions reported in Tables 1, 5, and 6.

Scheme 2



Daasbjerg[37] recently reported that the rate constant for product formation from diphenylethylsulfuranyl radical is 7×10^8 s^{-1}. Since we observed a quantum yield of 0.5 for product formation for the reductive cleavage of the closely related ditolylethylsulfonium salt **1** photosensitized by PA, we set the back electron transfer rate constant equal to the rate constant for product formation, 7×10^8 s^{-1}. This back electron transfer rate constant for the reaction of $\mathrm{PA}^{\bullet+}$ with ditolylethylsulfuranyl radical corresponds[38] to a Marcus reorganization energy of 1.77 eV. In related fashion, we used the Marcus equation to calculate rate constants for return electron transfer (k_{-1} and k_{-2} in Scheme 1) for different mediators reacting with the sulfuranyl radical derived from **2**. These rate constants were used in turn to simulate the variation in $\mathbf{F}_{\mathrm{corr}}$ with mediator potential shown in Figure 3. The best-fit simulation corresponded to a reorganization energy of 1.2 eV; experimental and calculated results for $\mathbf{F}_{\mathrm{corr}}$ are compared in Figure 4.

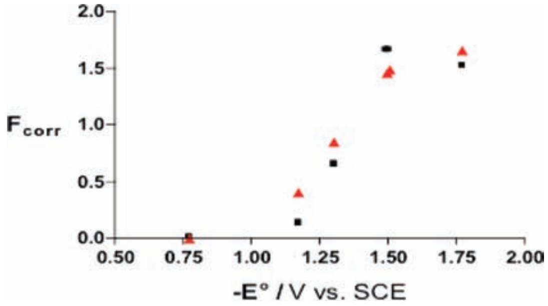


Figure 4. Experimental (red ▲) and calculated (black ■) product ratios $\mathbf{F}_{\mathrm{corr}}$ as a function of mediator potential for the indirect electrolyses of **2**-BF_4.

An alternative interpretation of the data is provided by Savéant's proposal that the mechanism of reductive bond

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[35] The rates of the forward and back electron transfer reactions of the sulfonium/sulfuranyl couple also depend on the nature of the redox partner. In the limit of exothermic reductions, the nature of the redox partner apparently does not have a significant effect on the relative rates k_1/k_2 and k_{-1}/k_{-2}, as judged by the small variations in **F**. On the other hand, the nature of the redox partner may account for some of the scatter in Figure 1.

[36] Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522–528.

[37] Vase, K. H.; Holm, A. H.; Norrman, K.; Pedersen, S. U.; Daasbjerg, K. *Langmuir* **2008**, *24*, 182–188.

[38] Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Reactivity and Structure Concepts in Organic Chemistry, Vol. 25; Springer-Verlag: Berlin, 1987; p 25.

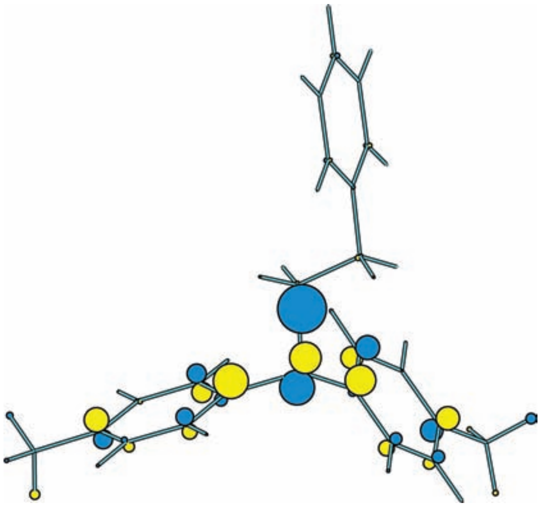

Figure 5. Coefficients on the atoms in the LUMO of compound **2.**

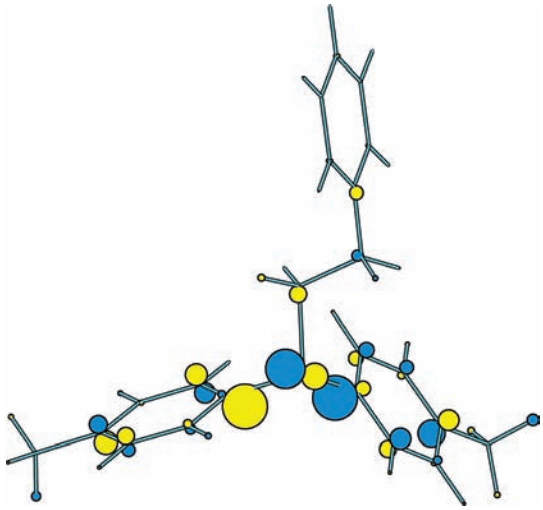

Figure 6. Coefficients on the atoms in the LUMO+1 of compound **2.**

cleavages can change from concerted to stepwise as the driving force for the electron transfer increases. In previous studies of the electrochemical reduction of sulfonium salts, Savéant observed both stepwise and concerted mechanisms as a function of the molecular structure of the sulfonium salt and identified borderline structures for which modest changes in driving force (~200 mV) led to changes in the mechanism.[21,39] Most recently, Daasbjerg used kinetic methods to detect a stepwise mechanism for the indirect electrolysis of diphenylethylsulfonium salt mediated by 4-methoxycarbonylazobenzene.[37] The experimental data correspond to an intermediate sulfuranyl radical with a lifetime of 1.4×10^{-9} s, which is long enough for the radical to escape the geminate-pair solvent cage.

In our thermal reactions, the structure of the sulfonium salt is constant, but the driving force changes by ~1 eV as the structure of the reducing agent changes. In the limit of regime I, the exothermic electron transfers correspond to large driving forces and a stepwise mechanism. Conversely, in the limit of regime III, the endothermic electron transfers correspond to small driving forces and a concerted mechanism. In effect, the reaction finds a concerted path because there is insufficient driving force to access the sulfuranyl radical intermediates. Between these two mechanistic limits, the concerted and stepwise mechanisms will compete in a ratio that changes with changing potential of the reducing agent; as the reduction potential of the mediator becomes more negative, the driving force for the electron transfer and the stepwise mechanism become more favorable.

The stepwise (regime I) and concerted (regime III) mechanisms give different limiting ratios of aryl and alkyl cleavage products (**F** ≈ 2.5 and 0, respectively). For any value of **F**, one can solve the simultaneous equations to estimate the mix of concerted and stepwise mechanisms. When F ≈ 0 (DCA, $E° = -0.77$ V), only alkyl cleavage is observed, corresponding to 100% concerted mechanism. When **F** = 0.4 (DCN, $E° = -1.17$ V), the mix of products and mechanisms corresponds to 60% concerted and 40% stepwise reactions. When the reducing agent is acetone radical anion ($E° = -2.4$ V), **F** = 2.5 and the mechanism is 100% stepwise. The stepwise mechanism identified[37] for the reduction of diphenylethylsulfonium ion by the radical anion of 4-methoxycarbonylazobenzene ($E° = -1.02$ V vs SCE) is presumably accompanied by an undetected concerted pathway. The products of the mediated reduction were not measured; based on Figure 3, we predict that the concerted cleavage to ethyl radical and diphenylsulfide is the major reaction.

It is clear that only the weaker S−alkyl bond will be broken in the concerted mechanism (**F** < 0.04). Therefore, a different mechanism (i.e., a stepwise mechanism) is required to break the stronger S−aryl bond. The stepwise mechanism is an essential component of both the kinetic and driving-force interpretations of the results. In the kinetic proposal, the mechanism is always stepwise. In the mixed-mechanism interpretation, stepwise and concerted mechanisms compete.[39] However, it cannot be the case that the stepwise mechanism gives only aryl cleavage. Were this true, only aryl cleavage would be observed in the limit of the strong driving forces in regime I. In fact, the stepwise mechanism in the limit of regime I gives a mixture of aryl and alkyl cleavage, with a preference for aryl cleavage (**F** ≈ 2.5). As discussed previously, sulfuranyl radical intermediates **j** and **k** rationalize the formation of alkyl and aryl cleavage products, respectively, and resolve the paradox that the presence of two aryl groups is a prerequisite for aryl cleavage.

The formation of **j** involves a change in alkyl-sulfur bonding, whereas the formation of **k** involves a change in the aryl-sulfur bonding. We used density functional theory (DFT) calculations to try to find the structures and energies of sulfuranyl radicals **j** and **k**. Unfortunately, the calculations failed to converge to minimized structures that did not contain a broken bond. The lowest-energy conformation for **2** in the gas phase and the coefficients on the atoms in the LUMO and LUMO+1 for that ground-state structure were obtained by DFT calculations. The coefficients on the atoms in the LUMO (Figure 5) clearly indicate the predominantly antibonding nature of the S−alkyl bond, with some involvement of the aryl π system. On the other hand, the coefficients on the atoms in the LUMO+1 (Figure 6) involve predominantly antibonding character in the S−aryl bond (along with the π system). According to these DFT calculations, the LUMO/LUMO+1 separation is modest (~0.5 eV).

While recognizing that these calculations apply to the starting sulfonium salt, we propose that the initial interaction of the reducing agent with the antibonding S−alkyl orbital

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[39] Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 4886–4895.

leads ultimately to sulfuranyl radical **j** and that the initial interaction with the antibonding S−aryl orbital leads ultimately to intermediate **k**. Since the permutational interconversion of these sulfuranyl radicals is slower than their fragmentation, the observed product ratio from the stepwise mechanism (**F** ≈ 2.5) reflects the relative populations (**k**/**j** ≈ 2.5). Because there are two ways to perturb the S−aryl bonding to form **k** but only one way to perturb the S−alkyl bonding to form **j**, the observed product ratio should be corrected for this statistical effect. Thus, the relative rate of formation of **k** is ∼1.25 times that of **j**, indicating that the activation energies leading to the two intermediates **j** and **k** are similar.

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Supporting Information Available: Characterization of the sulfonium cations **1** and **2** and the reaction products; experimental procedures for the photochemical, thermal, and mediated electrochemical reductions; simulation of the product ratios; and DFT calculations of the absolute energies and optimized geometry of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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