# Electrochemical Initiation of Aromatic $S_{RN}1$ Reactions Using Redox Catalysts[1]

James E. Swartz* and Timothy T. Stenzel

*Contribution from the Department of Chemistry, Grinnell College, Grinnell, Iowa 50112.
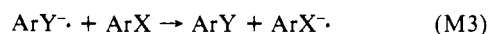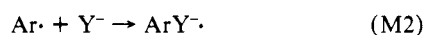Received September 26, 1983*

Abstract: Electrochemical reduction of benzonitrile in the presence of bromobenzene and tetra-N-butylammonium benzenethiolate in dimethyl sulfoxide (Me_2SO) forms diphenyl sulfide (67%) and benzene (38%). The reaction consumes 0.37 faraday per mol of bromobenzene, indicating that an $S_{RN}1$ chain reaction is occurring. Reaction in Me_2SO-d_6 gives a decreased yield of benzene (17%), 57% of which was monodeuterated, which along with coulometric data indicates that a major termination pathway is abstraction of hydrogen atoms from Me_2SO by phenyl radicals. Photoinitiated reactions in the presence and absence of tetra-N-butylammonium ions indicate that they are also a significant source of hydrogen atoms in termination. Evidence from reactions of 4-bromotoluene with benzenethiolate ion indicates that fragmentation of the diaryl sulfide radical anion intermediate is an important reaction in these systems. The presence of benzonitrile suppresses that cleavage.

Savéant has demonstrated the successful initiation of $S_{RN}1$ reactions of halonaphthalenes, halobenzophenones, and haloquinolines with a variety of nucleophiles.[2] For instance, benzenethiolate ion reacts with 4-bromobenzophenone when the potential of the cathode is set so that the aryl halide is reduced (reaction 1).[2a] The reaction consumes 0.2 faraday of electrons
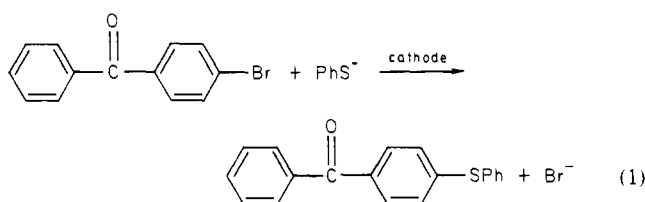
per mol of 4-bromobenzophenone, which requires a chain mechanism. The propagation sequence for the $S_{RN}1$ mechanism[3] proposed is sketched in Scheme I. A complete theoretical framework for understanding the kinetics of initiation, propagation, and termination steps has also been proposed.[1]
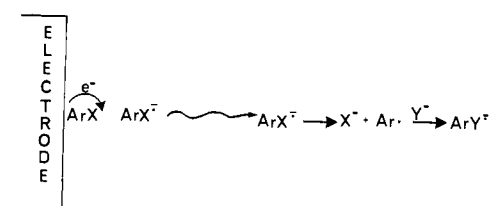
Scheme I. $S_{RN}1$ Mechanism

$$ArX^{-}\cdot \rightarrow Ar\cdot + X^{-} \qquad (M1)$$

$$Ar\cdot + Y^{-} \rightarrow ArY^{-}\cdot \qquad (M2)$$

$$ArY^{-}\cdot + ArX \rightarrow ArY + ArX^{-}\cdot \qquad (M3)$$
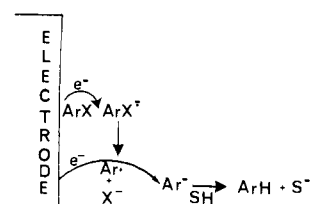
Preliminary Experiments and Proposal. In contrast to Savéant's results, our attempts to initiate the similar reactions of bromobenzene with benzenethiolate ion failed, forming almost entirely the hydrogen substitution product, benzene. Reduction of bromobenzene gave only an 8% yield of diphenyl sulfide, Ph_2S, and consumed 1.74 faraday per mol of bromobenzene. Benzene was the major product of the reaction. These results can be understood by considering the rate of fragmentation of the aryl halide radical anion. The relatively stable radical anions of halobenzophenones, quinolines, and naphthalenes are able to diffuse away from the electrode prior to cleaving to form aryl radicals and halide ion. This behavior is described in case I in Scheme II. Halobenzene radical anions, on the other hand, are known to cleave very rapidly (at or near the diffusion-controlled limit).[4] Such rapid cleavage
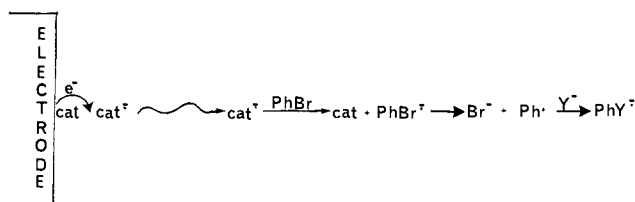
(1) Presented in part at the 184th National Meeting of the American Chemical Society, Kansas City, MO, September 1982; American Chemical Society, Washington, D.C.; Abstr. ORGN 95.

(2) (a) Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 1506. (b) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323 and references cited therein.

(3) (a) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (b) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 7463, 7464. (c) Rossi, R. A.; de Rossi, R. H. "Aromatic Substitution by the $S_{RN}1$ Mechanism"; American Chemical Society: Washington, D.C., 1983.

(4) M'Halla, F.; Pinson, J.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *89*, 347 and references cited therein.

Scheme II

results in the formation of phenyl radicals near the electrode surface where they are further reduced to phenyl anions (Scheme II, case II). Abstraction of a proton from the medium results in the formation of benzene and consumes two electrons per bromobenzene.

The key to electrochemical initiation of $S_{RN}1$ reactions of halobenzenes is to generate the halobenzene radical anion distant from the electrode surface where the phenyl radicals subsequently formed cannot be reduced and are available for reaction with a nucleophile. We report here the use of redox catalysts or electron carriers to initiate the $S_{RN}1$ reaction of bromobenzene with benzenethiolate ion.[5] The use of such redox catalysts is described in case III of Scheme II. The catalyst accepts an electron and diffuses away from the electrode to the bulk solution where it transfers the extra electron to bromobenzene. Cleavage of the bromobenzene radical anion forms phenyl radicals in a relatively

(5) After much of this work was completed, we were pleased to see the suggestion that it was possible appear in ref 3c, p 185.

Aromatic S_{RN}1 Reactions

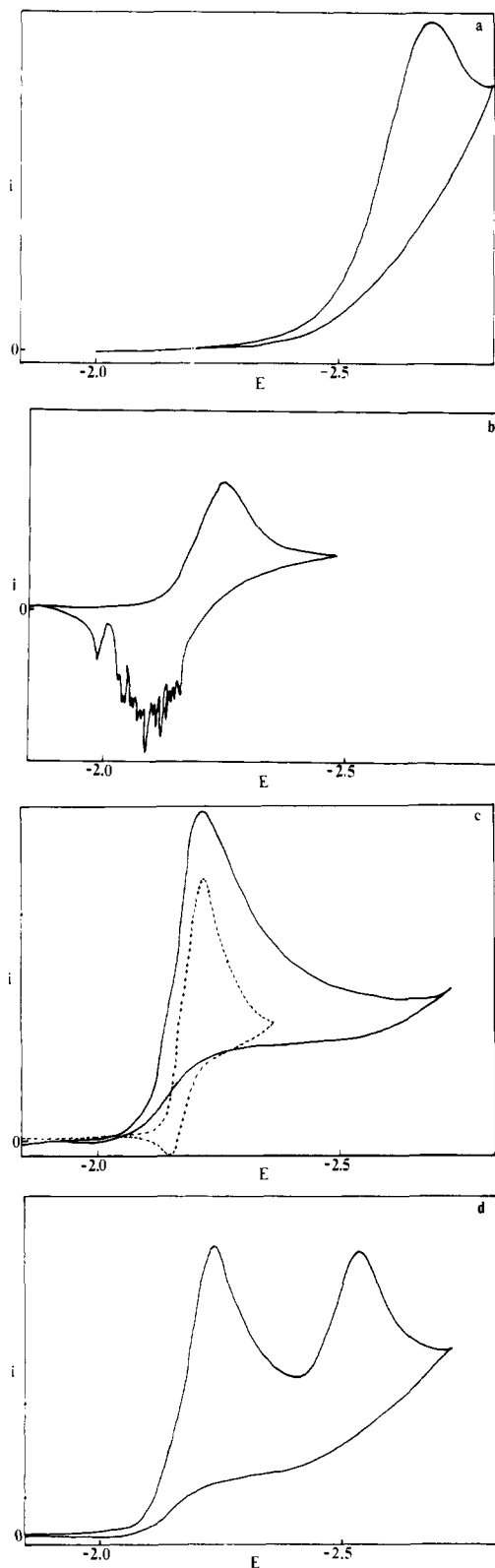*J. Am. Chem. Soc., Vol. 106, No. 9, 1984* 2521

Figure 1. Cyclic voltammograms in Me$_2$SO at a hanging mercury drop electrode, 0.1 M tetra-*N*-butylammonium perchlorate, Ag/AgCl reference electrode: (a) 2 mM bromobenzene; (b) 2 mM benzonitrile; (c) 2 mM bromobenzene, 2 mM benzonitrile; (—) 20 mV/s; (---) 200 mV/s; (d) 10 mM bromobenzene, 5 mM benzonitrile, 50 mM tetra-*N*-butylammonium benzenethiolate.

"nonreducing" medium where they can react with the nucleophile and initiate the S$_{RN}$1 chain reaction.

Results

Cyclic Voltammetry. The requirements of a successful redox catalyst are that it must be reduced positive of bromobenzene,

Table I. Electrochemically Initiated Reactions of Tetra-*N*-butylammonium Benzenethiolate with Bromobenzene

expt[a]	10^3[PhCN], M	faraday/ mole of PhBr consumed	% Ph$_2$S[b]	% PhH[b]	faraday/ mole of PhH formed
1[c]	0.0	1.74	8.0	93	1.87
2	5.6	0.82	66	54[d]	1.52
3	1.1	1.16	25	62	1.87
4	28.6	0.47	63	32	1.47
5[e]	5.6	0.31	56	37	0.84
6[e]	25.7	0.37	67	38	0.97
7[e,f]	5.18	0.18	68	17[g]	1.06

[a] All experiments conducted in Me$_2$SO, 1.0×10^{-2} M PhBr, 5.0×10^{-2} M TBA$^+$PhS$^-$, 0.1 M TBAP, Hg pool working electrode. Electrolysis at -2.2 V vs. Ag/AgCl. [b] Based on PhBr consumed. [c] Electrolysis at -2.5 V vs. Ag/AgCl. [d] GC analysis showed a substantial loss of PhCN. We suggest a two-electron reductive cleavage giving PhH. This would give the anomalously high Ph–H yield stated here since that yield is based on only PhBr consumed. [e] Cathode repeatedly pulsed on for 0.7 min/off for 4.3 min. [f] Solvent was (CD$_3$)$_2$SO. [g] 57% of the benzene was mono-deuterated.

be relatively stable in the radical anion form, and transfer an electron to bromobenzene at a resonable rate. We used the technique of cyclic voltammetry to measure reduction potentials and to examine, qualitatively, the catalyst stability and rate of the electron-transfer reaction. Figure 1a shows a cyclic voltammogram of bromobenzene in dimethyl sulfoxide (Me$_2$SO). The bromobenzene is reduced in a single two-electron wave at ca. -2.70 V. One possible catalyst examined was benzonitrile, which is reversibly reduced by one electron at -2.25 V (Figure 1b). Thus, benzonitrile fulfills two of the requirements of an appropriate redox catalyst; it is reduced positive of bromobenzene, and its radical anion does not spontaneously decompose in the solution. When bromobenzene is added to the solution there are several notable changes (Figure 1c). The benzonitrile reduction becomes irreversible, the bromobenzene reduction wave disappears, and the reduction current for benzonitrile increases. All these changes indicate that the benzonitrile radical anion is transferring an electron to bromobenzene (reaction 2).

$$PhCN^-\cdot + PhBr \rightarrow PhCN + PhBr^-\cdot \qquad (2)$$

At faster scan rates the benzonitrile reduction begins to become partially reversible. Benzonitrile satisfies all three requirements for a redox catalyst in our system. Cyclic voltammetry of a solution of benzonitrile, bromobenzene, and tetra-*N*-butylammonium benzenethiolate (TBA$^+$ PhS$^-$) showed the appearance of a new wave at -2.50 V, which corresponds to the reduction potential of diphenyl sulfide under these conditions (Figure 1d). This indicates the occurrence of the S$_{RN}$1 reaction of bromobenzene with benzenethiolate ion using benzonitrile as the redox catalyst as described in case III, Scheme II.

Preparative Experiments. Results of preparative electrolyses are summarized in Table I. From comparison of experiments 1 and 2 it is clear that the use of redox catalyst allows successful initiation of the chain reaction. The reaction forms a substantial yield of the substitution product, diphenyl sulfide, and consumes less than one electron per mol of bromobenzene used. A significant amount of the hydrogen substitution product, benzene, is, however, formed. We felt that a likely termination step was the reduction of phenyl radicals by benzonitrile radical anions (reaction 3). To

$$PhCN^-\cdot + Ph\cdot \rightarrow PhCN + Ph^- \qquad (3)$$

decrease the rate of this termination step we decreased the concentration of the catalyst, benzonitrile, which should result in a concomitant decrease in the benzonitrile radical anion concentration. To our surprise the yield of diphenyl sulfide decreased and the number of electrons consumed increased (experiment 3). An explanation of this behavior will be offered later, but at this time it is worthwhile to note that an increase in the benzonitrile concentration did not further increase the diphenyl sulfide yield (experiment 4), but it decreased the number of electrons consumed.

Table II. Photoinitiated Reaction of Potassium Benzenethiolate with Bromobenzene in Me$_2$SO-d_6[a,b]

expt	moles of PhBr used × 10^5	moles of TBAP used × 10^5	moles of Br$^-$ released × 10^5	% yield[c] of Ph$_2$S	% yield[c] PhH + PhD	PhD/ (PhH + PhD)
8[d]	4.80	0.0	3.84	42	16	0.91
9[e]	5.00	100	3.80	40	28	0.39

[a] See ref 8. [b] 5.0 × 10^{-2} M PhSK, irradiated for 60 min. [c] Based on Br$^-$ released. [d] PhSCD$_3$, 41% (based on Br$^-$), also detected. [e] PhSCD$_3$, 29% (based on Br$^-$), also detected.

In experiments 5 and 6 the electrode was pulsed on and off, anticipating that the chain reaction could be initiated when the electrode was on and would proceed while the electrode was off. This procedure should help to minimize the effect of termination via reaction 3. The yields of diphenyl sulfide and benzene remained relatively constant, but the number of electrons used further decreased.

The formation of diphenyl sulfide results from a chain reaction and does not consume electrons. The formation of benzene, on the other hand, is a termination step and does consume electrons. In experiments 5 and 6 only one electron is consumed per benzene formed, indicating that the benzene is formed in a one-electron process as in reaction 4. Reaction in Me$_2$SO-d_6 (experiment 7)

$$Ph\cdot + Z\text{--}H \rightarrow PhH + Z\cdot \qquad (4)$$
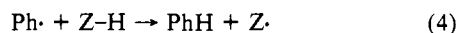
results in a decreased yield of benzene, 57% of which is monodeuterated, indicating eq 4 where Z = Me$_2$SO is a major termination pathway. Since 43% of the benzene is protonated, it is clear that some other source of hydrogen atoms must be present. We thought that thiophenol might be that source, but reaction in the presence of 10% excess tetra-N-butylammonium hydroxide over thiophenol resulted in virtual duplication of the results from experiment 7.

A photoinitiated reaction under the same conditions as experiment 7 but in the absence of tetra-N-butylammonium ions resulted in an 18% yield of benzene, 91% of which was monodeuterated (experiment 8, Table II). However, when tetra-N-butylammonium ions were present the benzene yield increased to 29%, only 40% of which was monodeuterated (experiment 9, Table II).

Rossi and co-workers have found evidence that the diphenyl selenide and diphenyl telluride radical anions fragment during photoinitiated S$_{RN}$1 reactions in refluxing ammonia.[6] There is, however, evidence that such fragmentation (the reverse of step M2) does not occur in reactions forming diaryl sulfide radical anions.[7] We felt that since our conditions (Me$_2$SO at room temperature) were substantially different, fragmentation could possibly occur. A photoinitiated reaction of benzenethiolate ion with 4-bromotoluene resulted in the formation of substantial amounts of diphenyl sulfide and benzene in addition to phenyl tolyl sulfide and toluene (experiment 10, Table III). These results provide clear evidence of such fragmentation. Interestingly the addition of the redox catalyst, benzonitrile (experiment 11, Table III), results in markedly decreased yields of the products derived from fragmentation of the tolyl phenyl sulfide radical anion.

Discussion

We clearly demonstrated the use of electrochemical redox catalysis to initiate aromatic S$_{RN}$1 reactions. Yields of substitution product are good but not quantitative. Extension of this approach to other aryl halides as well as to other nucleophiles is, in principle,

Table III. Photoinitiated Reaction of Potassium Benzenethiolate with 4-Bromotoluene in Me$_2$SO[a]

expt	10^3[PhCN] used, M	% PhSTol	% Ph$_2$S	% TolH	% PhH	(Ph$_2$S + PhH)/ (PhSTol + TolH)	(PhH + TolH)/ (Ph$_2$S + TolSPh)
10	0.0	14	5.0	37	35	0.78	3.79
11	6.4	53	10	20	5	0.21	0.40

[a] 1.0 × 10^{-2} M TolBr, 5.0 × 10^{-2} M PhSK, irradiated for 1 h.

possible. Qualification of an appropriate redox catalyst are that it be reversibly reduced positive of the aryl halide. We believe that the rate of electron transfer from the reduced catalyst to the aryl halide is important. If it is too rapid, electron transfer will take place close to the electrode surface where phenyl radicals can be further reduced. If it is too slow, the reduced catalyst concentration will have to be large and reduction of phenyl radicals by the reduced catalyst will begin to interfere with the chain reaction. No attempt was made to analyze the reaction kinetics in our system, but Savéant has reported the rate constant for reaction 2 to be 2 × 10^4 M^{-1} s^{-1} in dimethyl formamide at 22 °C.[9] We find that about 0.5-V separation between the cathodic peak potential of the catalyst and that of the aryl halide is a good rule of thumb for an effective catalyst.[10]

Photolysis is by far the most common method of initiation of aromatic S$_{RN}$1 reactions.[3] For instance, iodobenzene reacts with benzenethiolate ion in ammonia when stimulated by ultraviolet light to form diphenyl sulfide in nearly quantitative yield (equation 5).[11] Yields are typically high, but large-scale reactions are often

$$PhI + PhS^- \rightarrow Ph_2S + I^- \qquad (5)$$
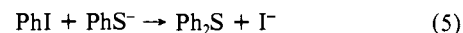
very slow, presumably due to light absorption by the products as they are formed. In addition bromo- and chlorobenzene reactions are substantially slower than iodobenzene reactions, sometimes to the extent that they do not react at all.[3] Initiation by solvated electrons in ammonia has been reported by Bunnett and co-workers for several systems.[12] Such initiation allows the use of any of the halobenzenes, but reactions typically result in low substitution product yields, forming the two-electron reduction product, benzene, and sometimes products resulting from the reductive decomposition of the substitution product.[13] Electrochemical initiation using redox catalysts should be effective for any halobenzene and, in principle, is more straightforward to scale up than photoinitiation. Redox catalysts have been used by several workers to investigate electron-transfer reactions which are inaccessible when other techniques are used. Savéant has used such catalysts to measure the reduction potentials of halobenzenes and pyridines.[8] Several workers have investigated the mechanism of alkyl halide reductions by using aromatic hydrocarbons as redox catalysts.[14] Redox catalysts have also found wide application in attempts to store solar energy as chemical energy.[15] As far as we know this is the first report of the use of electrochemical redox catalysis to initiate a chain reaction. Savéant and co-workers have reported the conceptually similar initiation of S$_{RN}$1 reactions by generation of ArY$^-\cdot$ at an electrode surface.[16]

Termination. At this point it is worthwile to comment on the number of electrons used per bromobenzene consumed. The

(6) Pierini, A. B.; Rossi, R. A. J. Org. Chem. 1979, 44, 4667.

(7) Bunnett, J. F.; Creary, X. J. Org. Chem. 1975, 40, 3740.

(8) PhSCH$_3$ appeared as a product in these photoinitiated reactions. We have not observed it as a product in other electrochemically or photochemically initiated reactions. We do not know whether this product is derived from phenyl radicals or benzenethiolate ion, but its addition to the mass balance equation for phenyl radicals is gratifying. Further investigation into the source of this product is in progress.

(9) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Savéant, J. M. J. Am. Chem. Soc. 1979, 101, 3431.

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Aromatic $S_{RN}1$ Reactions

J. Am. Chem. Soc., Vol. 106, No. 9, 1984 2523

formation of diphenyl sulfide results from a chain reaction and does not consume electrons. The formation of benzene, on the other hand, is a termination step and does consume electrons. Phenyl radicals can be reduced to phenyl anions at the electrode or via reaction 3.[17] This process forms benzene (after proton abstraction from the solvent or supporting electrolyte) by a two-electron process. Alternatively, phenyl radicals may abstract a hydrogen atom from the medium (reaction 4) which results in a one-electron process to form benzene. In experiments 2, 3, and 4, more than 1, but less than 2, faraday was consumed per mol of benzene formed, indicating a mixture of termination due to reactions 3 and 4. In experiments 5 and 6, however, only one electron is consumed per benzene formed, indicating that reaction 4 is the only significant pathway. Results from reaction in $Me_2SO\text{-}d_6$ indicate that a major termination pathway involves phenyl radicals abstracting hydrogen atoms from the Me_2SO (reaction 4, Z = Me_2SO). The low benzene yield in experiment 7 is likely to result from a decrease in the rate of reaction 4 in $Me_2SO\text{-}d_6$ due to the kinetic isotope effect. Savéant and co-workers have reported k_H/k_D for aryl radicals abstracting hydrogen atoms from Me_2SO to be in the range of 6–14.[18] Note that the amount of monodeuteriobenzene formed understates the amount of termination via hydrogen atom abstraction from the solvent in nondeuterated Me_2SO.

A possible source of nondeuterated benzene is hydrogen atom abstraction from thiophenol, a reaction which is known to be rapid.[19] Thiophenol could be formed by proton abstraction from residual water, but that equilibrium lies far on the side of the thiophenoxide ion.[20] A second source is protonation by the tetra-*N*-butylammonium ion (via Hofmann elimination). The experiment conducted with excess hydroxide ion present, however, appears to rule this out as a possibility.

A second possible source of the nondeuterated benzene in experiment 7 is hydrogen atom abstraction from the supporting electrolyte cation, tetrabutylammonium ion. The data in Table II indicate that in the absence of tetra-*N*-butylammonium ions, nearly all benzene is monodeuterated. When tetra-*N*-butylammonium ions are present the benzene yields as well as the ratio of monodeuterated to nondeuterated benzene are close to those in the electrochemically initiated reactions, indicating that tetra-*N*-butylammonium ions are a significant source of hydrogen atoms. These facts add further support for the theory that neither the catalyst nor the electrode are involved in termination.

A comment on the number of electrons consumed in the formation of benzene is appropriate. We assert that, since only one electron is consumed per benzene formed, hydrogen atom abstraction must be invoked. These results are, in fact, somewhat more puzzling than first meets the eye. Savéant has invoked hydrogen atom abstraction from the solvent as a major step in the reduction of some aryl halides in Me_2SO.[18,21] He reports, however, that most reductions consume two electrons per aryl halide molecule reduced. The second electron reduces the dimsyl radical (formed as the product of hydrogen atom abstraction) to dimsyl anion. In some cases where less than two electrons per aryl halide are consumed, Savéant suggests that the dimsyl anion reacts with aryl radicals by an $S_{RN}1$ mechanism. We searched for that substitution product (and its expected decomposition products) and were unable to find even a trace of it. In the direct reduction of aryl halides, aryl radicals, and thus dimsyl radicals, are formed close to the electrode surface. In our system, with redox catalysts and a chain reaction, the chemistry is likely to carry

the site of termination far away from the electrode surface where some other reactions which do not consume electrons effectively compete with reduction of dimsyl radicals. Similar effects of heterogeneity in solvated electron initiated $S_{RN}1$ reactions have been proposed by Bunnett.[22]
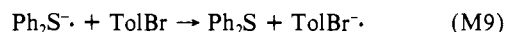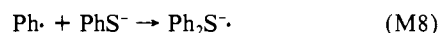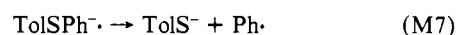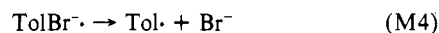
Effect of Redox Catalyst Concentration. From the preparative electrolysis experiments it can be concluded that there is some minimum benzonitrile concentration for achieving an efficient chain reaction. Increasing the benzonitrile concentration above 5 mM appears to have little effect on the course of the reaction, but decreasing it below that level had a deleterious effect. This behavior led us to inquire whether the catalyst had more than one role in the reaction. One possibility was that benzonitrile rather than bromobenzene may accept an electron from the diphenyl sulfide radical anion (reaction 6), and subsequently transfer an electron to bromobenzene (reaction 2) to continue the propagation sequence.

$$Ph_2S^{-}\cdot + PhCN \rightarrow Ph_2S + PhCN^{-}\cdot \qquad (6)$$
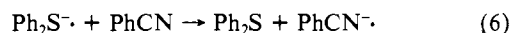
Cyclic voltammetry of diphenyl sulfide in Me_2SO indicates that its reduction is irreversible even at very fast scan rates. A recent report estimates the rate of cleavage of diphenyl sulfide radical anions to phenyl radicals and benzenethiolate ions (the reverse of reaction M2) in dimethyl formamide at 25 °C to be ca. 6 × $10^6 \ s^{-1}$.[23] Reaction M2 can thus be viewed as an equilibrium that equilibrium is bled off from the left side by reaction 4 and on the right side by reactions M3 and 6. An increase in the benzonitrile concentration increases the rate of reaction 6 and should decrease the steady-state concentration of phenyl radicals, decreasing the rate of termination via reaction 4.

To examine reactions for evidence of cleavage of the diphenyl sulfide radical anion, a photoinitiated reaction of 4-bromotoluene with potassium benzenethiolate was conducted in Me_2SO. A mixture of 4-tolyl phenyl sulfide and diphenyl sulfide was obtained as well as benzene and toluene (Table III). The formation of the scrambled product, diphenyl sulfide, can be explained with reference to Scheme III. The 4-tolyl phenyl sulfide radical anion

Scheme III

$$TolBr^{-}\cdot \rightarrow Tol\cdot + Br^{-} \qquad (M4)$$

$$Tol\cdot + PhS^{-} \rightarrow TolSPh^{-}\cdot \qquad (M5)$$

$$TolSPh^{-}\cdot + TolBr \rightarrow TolSPh + TolBr^{-}\cdot \qquad (M6)$$

$$TolSPh^{-}\cdot \rightarrow TolS^{-} + Ph\cdot \qquad (M7)$$

$$Ph\cdot + PhS^{-} \rightarrow Ph_2S^{-}\cdot \qquad (M8)$$

$$Ph_2S^{-}\cdot + TolBr \rightarrow Ph_2S + TolBr^{-}\cdot \qquad (M9)$$

can transfer an electron to 4-bromotoluene (reaction M6) and form the expected substitution product. Alternatively, it can fragment in either of two senses forming tolyl radicals and benzenethiolate ions (reverse of reaction M5) or phenyl radicals and 4-toluenethiolate ions (reaction M7). Reaction of those phenyl radicals with benzenethiolate ion (reaction M8) results in the formation of diphenyl sulfide. When the same reaction was conducted in the presence of benzonitrile, the yield of tolyl radical derived products (tolyl phenyl sulfide and toluene) increased significantly over the phenyl radical derived products (diphenyl sulfide and benzene) (see Table III). In addition the yield of hydrogen substitution products (toluene and benzene) was markedly lower in the presence of benzonitrile. These facts support our hypothesis that the redox catalyst, benzonitrile, is involved in reaction 6 as well as in reaction 2.

These results contrast with those of Bunnett and Creary,[7] who found no evidence of scrambling in the photoinitiated reaction

(17) Alternatively phenyl radicals can be reduced by $Ph_2S^{-}\cdot$, but this would give the same experimental results observable in our system as that of reaction 3. Savéant has denoted this step as DISP.[1]

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of 4-iodotoluene with benzenethiolate ion in liquid ammonia. Liquid ammonia has, however, been found to reduce the rate of fragmentation of aromatic radical anions with respect to a protic organic solvents at room temperature.[24] Rossi and Bunnett have reported evidence of similar fragmentation in reactions of alkanethiolate ions with phenyl halides.[7,25] Scrambling similar to that observed in our system has been reported by Rossi in reactions of phenyl telluride ion[6] and of anionic group 5 nucleophiles[26] with halobenzenes.

Experimental Section

General. Cyclic voltammetry and preparative electrolyses were conducted on Princton Applied Research Models 173 and 175. Coulometry was conducted by cutting and weighing current–time curves, by computer integration of current–time curves, or by using a PAR 179 digital coulometer. Cyclic voltammograms were recorded on a Houston Instruments Model 2000 x,y recorder or, for scan speeds >500 mV/s, a Nicolet Explorer III digitial oscilloscope. Standard, three-compartment cells were used for all electrochemical experiments. Cells were flushed with and kept under a positive pressure of nitrogen, which had been deoxygenated by passage through a hot copper trap at 500 °C. Cyclic voltammograms were recorded on a Metrohm E410 hanging mercury drop electrode or a 2-mm platinum wire sealed in a glass tube, ground flat, and polished with 0.3 μm alumina. Silver–silver chloride was used as a reference electrode, and all potentials are quoted with respect to this reference. A platinum wire served as a counter electrode.

Gas chromatography was conducted on a Hewlett-Packard 5992B gas chromatograph–mass spectrometer or a Hewlett-Packard 5880 gas chromatograph equipped with a flame ionization detector. Both instruments were equipped with 12-m fused-silica capillary columns coated with silicone oil. Injection ports and detector were maintained at 250 °C. Columns were operated at 6–250 °C. Quantitative analyses were conducted with toluene or fluorobenzene as internal standards for benzene and with biphenyl or naphthalene as standards for bromobenzene, benzonitrile, and diphenyl sulfide. In all cases, areas were corrected for molar response as determined from standard solutions of the products and the internal standard. Benzene–deuteriobenzene ratios were determined by a selected-ion monitoring program on the GCMS, assuming equal molar response and correcting for M − 1 and M + 1 peaks. Irradiations were conducted with a Rayonet RPR-100 photochemical reactor equipped with 16 lamps emitting maximally at 350 nm.

Materials. Triple-distilled mercury was obtained from Bethlehem Instruments. Dimethyl sulfoxide was purified by the method of Ritchie.[27] Tetra-*N*-butylammonium perchlorate (G. Frederick Smith) was dried under vacuum at 80 °C prior to use. Bromobenzene, benzonitrile, and 4-bromotoluene were used as obtained. Tetra-*N*-butylammonium hydroxide (40% aqueous) was purchased from Alfa Inorganics or Sigma Chemical. Deuterated Me$_2$SO (99.9% D) was purchased from Sigma or Aldrich and purified in the same manner as above. 4-Tolyl phenyl sulfide was prepared by the method of Bunnett and Creary.[5]

Electrochemically Initiated Reaction of Bromobenzene with Tetra-*N*-butylammonium Benzenethiolate in the Presence of Benzonitrile. Thiophenol (0.275 g, 0.0025 mol) was added to 40% aqueous tetra-*N*-butylammonium hydroxide (1.26 g, 0.0025 mol) in a 100-mL round-bottomed flask. The water was evaporated in vacuo on a Kuglerohr apparatus leaving a white solid. Nitrogen was bled into the flask, and the flask was capped with a septum. Tetra-*N*-butylammonium per-

chlorate (2.84 g, 0.01 mol) was added to a nitrogen-flushed 100-mL volumetric flask, and the flask was stoppered with a septum. Me$_2$SO, ca. 10 mL, was added to the flask containing the tetra-*N*-butylammonium benzenethiolate via a syringe, and the flask was swirled to effect dissolution. This solution was transferred to the volumetric flask which was then filled to the mark with Me$_2$SO. Fifty millileters of this solution was used to fill the nitrogen-flushed working electrode compartment of the electrochemical cell. The rest of the solution was divided between the counter and reference electrode compartments. The solution was preelectrolyzed at −2.50 V until the current decayed to a small, constant value which was used as a background to substract from the total charge passed. Bromobenzene (0.078 g, 5.0 × 10^{-3} mol) and benzonitrile (0.0288 g, 2.8 × 10^{-4} mol) were added, and nitrogen was bubbled through the solution to stir it. The working electrode was repeatedly turned on (−2.20 V) for 0.7 min and off for 4.3 min until 5.91 C had passed. Biphenyl and toluene were added as internal standards, and the solution from the working electrode compartment was added to 150 mL of H$_2$O. The resulting solution was extracted (3 × 100 mL) with ether and the combined ether phases were washed with 5% NaOH, 75 mL, and H$_2$O, 75 mL. The ether phase was dried and analyzed by GCMS. The products were identified by comparison of retention times and mass spectra to those of an authentic sample. The aqueous phase was acidified with HNO$_3$, extracted with ether (3 × 75 mL), made basic with 5% NaOH, and diluted to 500 mL. Aliquots, 50 mL, were treated with ca. 1 mL of 30% H$_2$O$_2$, acidified, and titrated with 0.007 M AgNO$_3$. Titration indicated 1.61 × 10^{-4} mol of bromide was released. Qualitative GC analysis gave the following results (percentages based on bromide ion released): diphenyl sulfide, 56%; benzene, 37%.

Potassium Benzenethiolate. Potassium hydroxide (8.42 g, 0.15 mol) was dissolved in 7 mL of water, and to this solution was added thiophenol (17.05 g, 0.155 mol). The mixture was extracted with ether (2 × 10 mL), and water was removed under nitrogen by azeotropic distillation with benzene in a Dean–Stark apparatus. Benzene was removed in vacuo, and the resulting salt was recrystallized from acetone and water. The potassium benzenethiolate was dried at 80 °C in vacuo.

Photoinitiated Reaction of *p*-Bromotoluene with Potassium Benzenethiolate in Me$_2$SO. Potassium benzenethiolate (0.0746 g, 5.0 × 10^{-4} mol) and 4-bromotoluene (0.0074 g, 4.3 × 10^{-5} mol) were added to a nitrogen-flushed, three-neck, 25-mL round-bottomed flask containing 10 mL of Me$_2$SO. The solution was stirred and placed in the photochemical reactor, and the lamps were turned on for 60 min. A solution containing internal standards, naphthalene (2.49 × 10^{-5} mol) and fluorobenzene (2.52 × 10^{-5} mol), was added. The reaction mixture was added to 30 mL of water, and the resulting solution was extracted with ether (3 × 20 mL). The combined ether phases were washed with 20 mL of 5% NaOH and 20 mL of water and dried with MgSO$_4$. The water phase was acidified with nitric acid, extracted with ether (3 × 20 mL), made basic, and treated with 30% H$_2$O$_2$ to oxidize any remaining thiols. Acidification and titration of the aqueous phase with 0.007 M AgNO$_3$ indicated 70.4% bromide ion released. Gas chromatographic analysis (HP 5880, 6–200 °C) indicated the following products (percentage based on bromide ion released): benzene, 35%; toluene, 37%; diphenyl sulfide, 5.4%; phenyl tolyl sulfide, 14%.

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