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Very Fast, in Cage, Recombination of a Radical with a Nucleophile. Arylazo Sulfides in $S_{RN}1$ Aromatic Nucleophilic Substitutions

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The cyclic voltammograms of (*E*)-(4-cyanophenyl)azo (**1a**) and (*E*)-(4-nitrophenyl)azo phenyl sulfide (**1b**) as well as of (*E*)- and (*Z*)-(4-cyanophenyl)azo *tert*-butyl sulfide [(*E*)-**1c** and (*Z*)-**1c**] evidence an extremely effective recombination between the aryl radical and the thiolate anion originating from the decomposition of the radical anions of the azo sulfides. Solvent changes and the addition of CN^- as an "external" nucleophile point to a cage effect as the cause of such efficient $S_{RN}1$ reactions leading to the corresponding aryl phenyl or aryl *tert*-butyl sulfides **2a–c**. In the case of (4-cyanophenyl)-azo *tert*-butyl sulfide [(*E*)-**1c** and (*Z*)-**1c**], trapping by the "external" nucleophile is more efficient with the (*E*)-isomer than with the (*Z*)-isomer, and the possible causes of this effect are discussed.

The $S_{RN}1$ mechanism of aromatic nucleophilic substitution is a chain process involving as the key step the coupling of an aryl radical with an anionic nucleophile.[2,3] Most of the substrates used in these reactions are represented by aryl halides; more recently, azo sulfides **1** have been shown[4] to be interesting starting compounds because of both a favorable reduction potential and a facile fragmentation of the radical anions. In the absence of an added ("external") nucleophile, the thiolate anion, itself obtained by concerted cleavage[5] of C–N and N–S bonds

$$\underset{1}{\mathrm{ArN{=}NSR}} + \text{electron donor} \rightleftharpoons \mathrm{ArN{=}NSR^{\bullet-}} \tag{1}$$

$$\underset{1^{\bullet-}}{\mathrm{ArN{=}NSR^{\bullet-}}} \xrightarrow{k_2} \mathrm{Ar^{\bullet}} + \mathrm{N_2} + {}^{-}\mathrm{SR} \tag{2}$$

$$\mathrm{Ar^{\bullet}} + {}^{-}\mathrm{SR} \xrightarrow{k_3} \underset{2^{\bullet-}}{\mathrm{ArSR^{\bullet-}}} \tag{3}$$

$$\underset{2^{\bullet-}}{\mathrm{ArSR^{\bullet-}}} + \mathrm{ArN{=}NSR} \rightleftharpoons \underset{2}{\mathrm{ArSR}} + \mathrm{ArN{=}NSR^{\bullet-}} \tag{4}$$

1a, 2a Ar = 4-CNC_6H_5 R = C_6H_5
1b, 2b Ar = 4-$NO_2C_6H_5$ R = C_6H_5
1c, 2c Ar = 4-CNC_6H_5 R = ^{t}Bu
1d, 2d Ar = 4-$NO_2C_6H_5$ R = ^{t}Bu

in the radical anion $1^{\bullet-}$ (reaction 2), behaves (reaction 3) as an "internal" nucleophile toward the aryl radical resulting from the same fragmentation. The final product is the sulfide **2** obtained by the reoxidation of its radical anion $2^{\bullet-}$ (reaction 4). The electron donor in reaction 1 can be an excess of thiolate, an electrode, or an appropriate reductant/nucleophile acting either spontaneously or under photostimulation.

The exploitation of the azo sulfides **1** (and hence of the parent arylamines) as starting materials for the $S_{RN}1$ synthesis of various functionalized aromatic compounds hinges on the possibility to use "external" nucleophiles able to effectively compete (reaction 3′) for the $Ar^{\bullet}$ radical.

$$\mathrm{Ar^{\bullet}} + \mathrm{Nu^-} \xrightarrow{k_{3'}} \mathrm{ArNu^{\bullet-}} \tag{3′}$$

Formation of $ArNu^{\bullet-}$ triggers a new propagation cycle leading to the synthetic target ArNu (reaction 4′).

$$\mathrm{ArNu^{\bullet-}} + \mathrm{ArN{=}NSR} \rightleftharpoons \mathrm{ArNu} + \mathrm{ArN{=}NSR^{\bullet-}} \tag{4′}$$

Several "external" nucleophiles have successfully been used including cyanide,[4b] aryl oxides,[4c] and carbanions.[4d,e] In agreement with the above equations it has been observed, for instance, that the photon- or electron-induced reactions of arylazo phenyl sulfides (**1**, R = Ph) with tetrabutylammonium cyanide give both aryl phenyl sulfides and aryl cyanides whose relative yields depend on the initial ratio between the substrate and the "external" nucleophile. As a matter of fact, an increase in the cyanide concentration leads to an enhanced nitrile yield accompanied by a decrease in the sulfide yield which is less than linear, i.e., pointing to a non-zero limit.[4b] This result could be indicative of a coupling of $Ar^{\bullet}$ and PhS^- (reaction 3) in the solvent cage.

Electrochemistry has proved to be a very efficient way of initiating and analyzing $S_{RN}1$ mechanisms.[6] In this case, the electron donor in reaction 1 is the cathode (either

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[5] The results obtained in the present paper (see below) suggest that the fragmentation of $1^{\bullet-}$ cannot significantly occur via stepwise mechanism through transient aryldiazenyl radicals.

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directly or through a suitable mediator) and the reoxidation of the radical anions of the substitution products can also take place at the same electrode (reactions 5 and 5′):

$$\mathrm{ArSR^{\bullet -} - e^- \rightleftharpoons ArSR} \qquad (5)$$

$$\mathrm{ArNu^{\bullet -} - e^- \rightleftharpoons ArNu} \qquad (5')$$

The mechanism is an overall zero-electron process, and the decrease toward zero of the first cathodic voltammetric peak of the substrate upon addition of increasing concentrations of nucleophile is one of the easiest ways to characterize the occurrence and the efficiency of an $S_{RN}1$ process. However, the coupling with the nucleophile is not the only reaction that aryl radicals can undergo: hydrogen atom transfer (6) from the solvent followed by reduction (7) of the resulting $S^\bullet$

$$\mathrm{Ar^\bullet + SH \rightarrow ArH + S^\bullet} \qquad (6)$$

$$\mathrm{S^\bullet + e^- \rightarrow S^-} \qquad (7)$$

and further reduction at the electrode (8) or in solution (9–11)

$$\mathrm{Ar^\bullet + e^- \rightarrow Ar^- \rightarrow ArH} \qquad (8)$$

$$\mathrm{Ar^\bullet + ArN{=}NSR^{\bullet -} \rightarrow Ar^- + ArN{=}NSR} \qquad (9)$$

$$\mathrm{Ar^\bullet + ArSR^{\bullet -} \rightarrow Ar^- + ArSR} \qquad (10)$$

$$\mathrm{Ar^\bullet + Ar\text{-}Nu^{\bullet -} \rightarrow Ar^- + ArNu} \qquad (11)$$

are the most important two-electron consuming side reactions. The number of electrons ($0 \leq n \leq 2$) consumed in the overall process thus represents a measure of the competition between reactions 3 + 3′ and reactions 6–11.

It is the aim of this paper to take advantage of the easy characterization of the $S_{RN}1$ process by cyclic voltammetry to investigate the competition between the "internal" (reaction 3) and the "external" nucleophile (reaction 3′) to assess the occurrence of reaction 3 as a cage process. To this end we report herein on the cyclic voltammetry of representative azo sulfides such as (4-cyanophenyl)azo (**1a**) and (4-nitrophenyl)azo phenyl sulfide (**1b**) (which only exist as (*E*)-isomers) as well as both (*Z*)- and (*E*)-(4-cyanophenyl)azo[7] (**1c**) and (4-nitrophenyl)azo (**1d**) *tert*-butyl sulfides.

Results

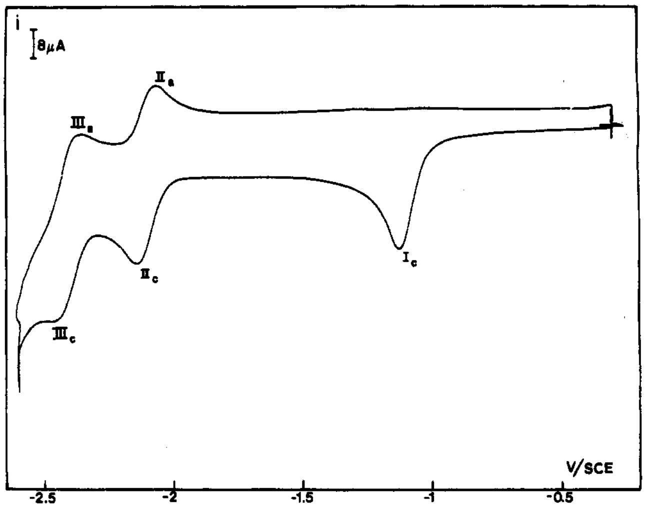

Figure 1. Cyclic voltammogram of **1a** (c = 1 mM) in ACN + 0.1 M $\mathrm{NBu_4ClO_4}$, GC electrode, reference SCE, scan rate v = 0.2 V s^{-1}.

The voltammogram of **1a** at 0.2 V/s^{-1} in acetonitrile (ACN) on a glassy carbon (GC) electrode (Figure 1) shows three reduction peaks. The first cathodic peak, located at E_p(Ic) = −1.12 V/SCE, is relevant to the irreversible reduction of **1a**, and its height (measured by reference to the monoelectronic wave of terephthalonitrile) corresponds to the consumption of 0.53 e^- per molecule. The reversible system IIc/IIa which appears at $E°$(IIc/IIa) = −2.08 V/SCE corresponds to the first peak of 4-cyanophenyl phenyl sulfide (**2a**) as shown by comparison with an authentic sample. The likewise reversible IIIc/IIIa system at $E°$ = −2.35 V/SCE corresponds to the second peak of **2a**, although it would be difficult to distinguish it from the first reversible system of any benzonitrile formed. A similar voltammogram is observed on a mercury electrode which also allows the detection of the oxidation peak of $\mathrm{C_6H_5S^-}$ and, on the second scan, the reduction peak of the so-formed $\mathrm{C_6H_5SSC_6H_5}$. Peak Ic shifts to negative potentials by 30 mV per log v (v = scan rate) indicating a first-order reaction following the electron transfer.[8] By increasing the scan rate to $v = 1.8 \times 10^4$ V s^{-1} using a 17-μm gold microelectrode, peak Ic becomes reversible enabling us to measure the redox potential $E°(\mathbf{1a}/\mathbf{1a}^{\bullet -})$ = −1.19 V/SCE and to evaluate the rate constant[9] for the decomposition of $\mathbf{1a}^{\bullet -}$: $k_2 = 2.7 \times 10^4$ s^{-1}. In dimethyl sulfoxide (DMSO) on a GC cathode one can again observe peak Ic at E_p(Ic) = −1.02 V/SCE (corresponding to 0.93 e^- per molecule) and the two reversible systems relevant to **2a** already detected in ACN, [$E°$(IIc/IIa) = −1.98 V/SCE and $E°$(IIIc/IIIa) = −2.28 V/SCE], but in addition, a new reversible system appears at $E°$ = −1.80 V/SCE which corresponds to the first reduction peak of bis(4-cyanophenyl) sulfide **3a** as shown by comparison with an authentic sample.[10] Upon increasing the scan rate to 400 V s^{-1} this system disappears while the IIc/IIa and IIIc/IIIa systems are still visible, indicating that **3a** is not a primary product from the reduction of **1a** but, most likely, the result of a further reaction of $\mathbf{2a}^{\bullet -}$.

In regard to the cyclic voltammetry of **1b**, in ACN on a GC electrode the first irreversible reduction peak is

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(10) Bis(4-cyanophenyl) sulfide **3a** presents, in DMSO, a first reversible system at $E°$ = −1.80 V/SCE followed by a second reversible system at $E°$ = −2.27 V/SCE (the cathodic peak being preceded by a spiky prepeak). This second reversible system cannot be distinguished from IIIc/IIIa pertaining to **2a** or to benzonitrile. (b) It is conceivable that **3a** arises from a fragmentation, much more marked in DMSO than in ACN, of the intermediate $\mathbf{2a}^{\bullet -}$ at the level of the sulfur–phenyl bond. Consistently, in the frame of $S_{RN}1$ processes, the ensuing 4-cyanobenzenethiolate anion (competing with benzenethiolate for the 4-cyanophenyl radicals, i.e., R = $\mathrm{4\text{-}CNC_6H_4}$ vs R = Ph in reaction 3, Ar = $\mathrm{4\text{-}CNC_6H_4}$) would lead to $\mathbf{3a}^{\bullet -}$ and eventually to **3a**. However, it is intriguing that the sulfide **3a** is not found among the products after a controlled potential electrolysis of **1a** in DMSO; this could be indicative of some instability of $\mathbf{3a}^{\bullet -}$ on the time scale of an electrolysis.

Table I. Cyclic Voltammetry Data for (*E*)- and (*Z*)-(4-Cyanophenyl)azo *tert*-Butyl Sulfides [(*E*)-1c and (*Z*)-1c]

	$E_p(\mathrm{Ic})^a$ (V/SCE)	$E°(\mathrm{Ic/Ia})^a$ (V/SCE)	n^b	k_2 (s^{-1})	$E_p(\mathrm{IIc})^a$ (V/SCE)
(*E*)-**1c**	–1.32	-1.31^c	0.81	10^3	-2.10^d
(*Z*)-**1c**	–1.34	-1.35^e	0.82	400	-2.10^d

[a] On a GC electrode at $v = 0.2$ V s^{-1}. [b] Number of electrons transferred at the level of peak Ic measured by rotating disk voltammetry. [c] The reversibility is observed at 500 V s^{-1}. [d] Reduction peak of 4-cyanophenyl *tert*-butyl sulfide (**2c**). [e] The reversibility is observed at 50 V s^{-1}.

Table II. Electron consumption[a] at the level of peak Ic of 1a and 1b

	ACN	DMF	PhCN	DMSO
η^b	3.75	8.45	12.8	24.7
k_H rel[c]	2.3	14.1	0^d	1
1a	0.53	0.87	0.53	0.93
1b	0.71	0.84	0.53	0.93

[a] On a GC electrode, by reference to terephthalonitrile. [b] Viscosity in mp (from ref 14). [c] Relative H atom donating ability towards phenyl radicals. Data from ref 15. [d] See text.

located at $E_p(\mathrm{Ic}) = -0.82$ V/SCE, the height corresponding to 0.71 e^- per molecule. Peak Ic is followed by the first reversible peak of 4-nitrophenyl phenyl sulfide (**2b**) [$E°(\mathbf{2b}/\mathbf{2b}^{\bullet-}) = -1.04$ V/SCE (by comparison with an authentic sample)], by the reversible peak of nitrobenzene ($E° = -1.13$ V/SCE), by the second irreversible peak of **2b** $E_p(\mathrm{IIIc}) = -1.90$ V/SCE, and finally by the second irreversible peak of nitrobenzene ($E_p = -2.20$ V/SCE). On a mercury cathode, a similar voltammogram is observed with, in addition, the oxidation peak of $C_6H_5S^-$. At a scan rate of 500 V s^{-1} on a mercury electrode the first peak of **1b** becomes reversible allowing the redox potential $E°(\mathbf{1b}/\mathbf{1b}^{\bullet-}) = -0.88$ V/SCE to be measured. The rate constant for the cleavage of $\mathbf{1b}^{\bullet-}$ can be obtained from the E_p/log v plot:[8] $k_2 = 75$ s^{-1}. The formation of 4-nitrophenyl phenyl sulfide and nitrobenzene is in agreement with the results of the reported electrolysis[4a] of **1b**.

Cyclic voltammetry of (*E*)-(4-cyanophenyl)azo *tert*-butyl sulfide (*E*)-**1c** evidences, in ACN on a GC electrode at 0.2 V s^{-1}, a first irreversible peak Ic at $E_p = -1.32$ V/SCE corresponding to the consumption of 0.81 e^- per molecule. At more negative potential [Ep(IIc) = –2.10 V/SCE] one observes an irreversible peak pertaining to 4-cyanophenyl *tert*-butyl sulfide (**2c**). By increasing the scan rate to $v = 500$ V s^{-1}, peak Ic becomes reversible and it is possible to measure[8] the rate constant for the cleavage of the radical anion (*E*)-$\mathbf{1c}^{\bullet-}$ $k_2 = 10^3$ s^{-1}. The voltammetric pattern of (*Z*)-**1c** is similar to that of (*E*)-**1c**: relevant data for both isomers are summarized in Table I.

The behavior of (*Z*)- and (*E*)-(4-nitrophenyl)azo *tert*-butyl sulfide [(*Z*)-**1d** and (*E*)-**1d**] is different, as in ACN on a GC electrode at $v = 0.2$ V s^{-1}, both isomers present a first reversible monoelectronic peak at $E°(\mathrm{Ic/Ia}) = -0.93$ V/SCE indicating that their radical anion is stable on the time scale of slow scan cyclic voltammetry; as a consequence, no peak can be observed which would correspond to the formation of 4-nitrophenyl *tert*-butyl sulfide **2d**.[11]

Changes of solvent viscosity have often been used to demonstrate the occurrence of cage effects, geminate recombinations increasing with the viscosity[12] (although solvation effects have often clouded the interpretations placed on the rate–viscosity correlations). Herein a more effective recombination of the aryl radical with the thiolate anion (reaction 3) in the solvent cage should be monitored by a decrease in the number of electrons involved in the overall process. However, a change of solvent may also alter the rate of reactions 6 and 7.

As the height of peak Ic is a criterion of the efficiency of the chain reaction, for **1a** and **1b**, the number of electrons transferred at the level of peak Ic has been measured in four solvents, ACN, DMSO, dimethylformamide (DMF), and benzonitrile (PhCN),[13] for comparison with ACN. The results obtained on glassy carbon electrodes are reported in Table II, along with the viscosity of the solvents[14] and their relative hydrogen atom donating ability toward phenyl radicals.[15] Most interestingly, the wave Ic always corresponds to a consumption of less than 1 e^- per molecule.

We also investigated the effect of adding an "external" nucleophile which could scavenge the aryl radicals. We chose cyanide, which has been shown to react with aryl halides[16] and azo sulfides[4b] in the course of $S_{RN}1$ reactions, for the following reasons: (i) the rate of coupling between 4-cyanophenyl radical and CN^- has been measured[16] in liquid ammonia at –40 °C ($k_{CN^-} = 3.1 \times 10^7$ M^{-1} s^{-1}); (ii) such coupling would eventually lead to terephthalonitrile (**4** (reactions 3″ and 4″), whose peak can be easily identified in the voltammogram of **1a**; and (iii) tetraethylammonium cyanide, used as an "external" nucleophile, is easily soluble both in ACN and in DMSO.

$$4\text{-NCC}_6H_4^{\bullet} + CN^- \xrightarrow{k_{CN^-}} 4\text{-NCC}_6H_4CN^{\bullet-} \qquad (3'')$$

$$4\text{-NCC}_6H_4\text{-}CN^{\bullet-} - e^- \rightarrow 4\text{-NCC}_6H_4CN \qquad (4'')$$

Upon addition of increasing amounts of CN^- the voltammogram of **1a** in ACN undergoes significant modifications (Figure 2): (i) the height of peak Ic decreases and becomes nearly zero for [CN^-] = 320 mM; (ii) the new reversible system IVc/IVa ($E°(\mathrm{IVc/IVa}) = -1.60$ V/SCE) corresponding to terephthalonitrile (**4**) increases in height up to a value corresponding to 0.83 e^- per molecule; and (iii) the height of peak IIc, which is related to the reduction of the sulfide **2a**, decreases to about 0.13 e^- per molecule

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(11) The second peak of (*Z*)-**1d** and (*E*)-**1d** ($E_p = -1.40$ V/SCE) is bielectronic, and on the reverse scan an anodic peak is observed at $E_{\mathrm{pa}} = -1.09$ V/SCE which is located at the same position as the anodic peak related to the reoxidation of nitrobenzene radical anion. The third peak observed in the cyclic voltammogram of (*Z*)-**1d** and (*E*)-**1d** can be assigned to the second wave of nitrobenzene. These voltammograms indicate that the radical anions (*Z*)- and (*E*)-$\mathbf{1d}^{\bullet-}$ are stable, while the dianions decompose to give eventually nitrobenzene which at the same potential is transformed into the corresponding radical anion; the latter is further reduced at the level of the third peak.

(12) Koenig, T.; Fischer, H. Cage effects. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, p 157.

(13) (a) To further test the influence of the medium viscosity on the consumption of electricity at the level of peak Ic, the effect of addition of glycerol ($\eta = 9450$ mp at 20 °C) was studied. No unambiguous result could, however, be obtained in this mixed solvent as, even if peak Ic decreases that of ferrocene used as a standard[13b] decreases far more quickly: thus, while peak Ic of **1a** corresponds to the consumption of 0.90 e^- per molecule in pure DMF a value as high as 3.17 e^- per molecule was observed in 50/50 (v/v) DMF/glycerol. No significant results could be obtained by shifting from DMSO to the more viscous dibutyl sulfoxide (at 36 °C). (b) Ferrocene was used as a standard because, in the mixed solvent, its peak remains reversible up to high concentrations of glycerol.

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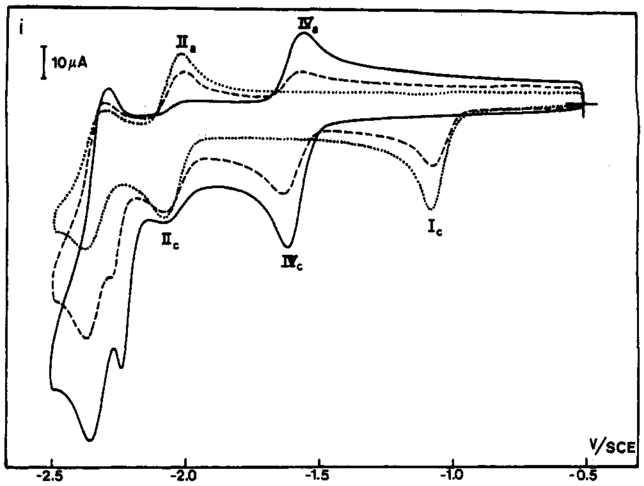

Figure 2. Cyclic voltammogram of **1a** (c = 1 mM) in ACN + 0.1 M NBu_4ClO_4 on a GC electrode, reference SCE, v = 0.2 V s^{-1}: (a) [CN^-] = 0 mM, ···; (b) [CN^-] = 10 mM, - - -; (c) $c(CN^-)$ = 320 mM —.

Table III. Height of the Peaks of 1a and 4 upon Addition of NEt_4CN in ACN[a]

[CN^-] (mM)	ip(Ic)[b] (μA)	ip(IVc)[b] (μA)	height of the peak in F/mol[c] Ic	IVc
0	40.4	0	0.53	0
0.9	39.3	1.6	0.49	0.02
2.8	34.8	7.2	0.43	0.09
4.3	31.6	11.6	0.39	0.14
6.5	26.4	18	0.33	0.22
8.8	23.2	23.2	0.29	0.29
10.0	21.4	26.8	0.27	0.33
21.0	15.2	39.2	0.19	0.49
47.0	8.8	53.6	0.11	0.67
100	4.8	61.6	0.06	0.77
210	2.4	65.6	0.03	0.82
320	0.8	66.4	0.01	0.83

[a] On a glassy carbon electrode. [b] Current of the first peak of **1a** (Ic) and of terephthalonitrile (**4**) (IVc). [c] By reference to terephthalonitrile.

at the highest concentration of CN^-. The last peak on the voltammogram, preceded by a prepeak, is relevant to the second reduction of **4** as confirmed by comparison with an authentic sample; it overlaps the second reduction of **2a**. The results for peaks Ic and IVc are gathered in Table III.

Similar results are obtained in DMSO: (i) peak Ic decreases to zero for [CN^-] = 220 mM; (ii) the height of IVc (relevant to terephthalonitrile) reaches 0.57 e^- per molecule; and (iii) the height of the cathodic peak of both **3a** and **2a** decreases to about 0.14 e^- per molecule. The results for peaks Ic and IVc are shown in Table IV.

In order to confirm the results obtained by cyclic voltammetry, electrolyses of **1a** (1 mM) were performed in the presence of 0.253 M tetraethylammonium cyanide both in ACN and in DMSO and the yields measured by HPLC. The results reported in Table V are in fair agreement with those obtained by cyclic voltammetry[10b] and with those previously obtained[4b] on a platinum cathode (20% yield of **2a** and 71% of **4**).

We also examined the voltammograms of (*E*)- and (*Z*)-**1c**, in the presence of increasing concentrations of cyanide. For (*E*)-**1c**, upon addition of 0.228 M NEt_4CN, the height of peak Ic decreases to 0.08 e^- per molecule while peak IVc, related to **4**, increases to 0.96 e^- per molecule. The results are shown in Table VI.

Table IV. Height of the Peaks of 1a and 4 upon Addition of NEt_4CN in DMSO[a]

$c(CN^-)$ (mM)	ip(Ic)[b] (μA)	ip(IVc)[b] (μA)	height of the peak in F/mol[c] Ic	IVc
0	19.2	0	0.93	0
0.9	16.6	0.6	0.80	0.03
3.3	14.4	2.2	0.69	0.10
5.5	11.5	4.3	0.55	0.21
10	9.3	5.4	0.45	0.26
17	7.4	7.4	0.35	0.35
28	5.8	9.9	0.28	0.45
51	3.5	10.9	0.17	0.52
67	1.9	11.5	0.09	0.55
88	1.8	11.8	0.08	0.57
130	0.9	11.8	0.05	0.57
170	0.6	11.8	0.03	0.57
220	0	11.8	0	0.57

[a–c] See corresponding footnotes of Table III.

Table V. HPLC Yields from Electrolyses of 1 mM 1a in the Presence of 0.253 M Et_4NCN

compd	yield in ACN (%)	yield in DMSO (%)
recovered azo sulfide **1a**	6.0	4.0
benzonitrile	traces	9.5
4-cyanophenyl phenyl sulfide (**2a**)	8.5	13.0
terephthalonitrile (**4**)	80.0	64.0

Table VI. Height of the Peaks of (*E*)-1c and 4 upon Addition of NEt_4CN in ACN[a]

[CN^-] (mM)	ip(Ic)[b] (μA)	ip(IVc)[b] (μA)	height of the peak in F/mol[c] Ic	IVc
0	45.6	0	0.66	0
0.6	46.0	2.4	0.66	0.03
2.6	43.0	10.4	0.62	0.15
7.1	40.0	22.4	0.58	0.32
15.9	30.4	39.4	0.44	0.57
42.5	19.2	54.4	0.28	0.79
89.7	12.0	65.6	0.17	0.94
144.0	5.5	66.0	0.08	0.95
228.0	5	66.4	0.08	0.96

[a] On a glassy carbon electrode. [b] Current of the first cyclic voltammetry peak of (*E*)-**1c** (Ic) and of terephthalonitrile (**4**) measured. [c] By reference to terephthalonitrile.

Table VII. Height of the Peaks of (*Z*)-1c and 4 upon Addition of NEt_4CN in ACN[a]

[CN^-] (mM)	ip(Ic)[b] (μA)	ip(IVc)[b] (μA)	height of the peak in F/mol[c] Ic	IVc
0	42.4	0	0.70	0
0.5	41.6	1.6	0.69	0.03
2.1	38.4	4.8	0.64	0.08
6.1	33.2	10.4	0.55	0.17
19.0	18.0	16.8	0.29	0.27
47.9	8.8	30.4	0.15	0.50
171.0	7.6	36.8	0.13	0.61
242.0	4.8	40.0	0.08	0.66
416.0	3.2	40.8	0.035	0.67
saturated	1.6	39.2	0.02	0.65

[a] On a glassy carbon electrode. [b] Current of the first cyclic voltammetry peak of (*Z*)-**1c** (Ic) and of terephthalonitrile (**4**). [c] By reference to terephthalonitrile.

Interestingly, different results are obtained for (*Z*)-**1c**; the height of peak Ic decreases to 0.02 e^- per molecule, while the first peak of terephthalonitrile (**4**) increases only to 0.65 e^- per molecule, as shown in Table VII.

Discussion

It has been shown previously[6] that the height of the cathodic peak of the substrate is a measure of the efficiency of an electrochemically induced $S_{RN}1$ process. Such height should decrease toward zero as the efficiency of the process increases because an overall zero-electron consumption is implied by reactions 1–5′. Actually, the most striking feature of the voltammograms of **1a** and **1b** is the particular smallness of the first reduction wave, taking also into account that the concentration of the nucleophile PhS^- cannot exceed that of the radical $Ar^{\bullet}$. For comparison sake, while in the case of **1a** the first wave represents a consumption of 0.53 e^- per molecule in ACN, we have observed that the addition of 1 equiv of tetramethylammonium benzenethiolate to a 1 mM solution of 4-bromobenzonitrile in ACN does not significantly decrease the reduction peak of the substrate.

A deeper insight into the system, aimed at ascertaining the reason for such a low current consumption, can be achieved by examining the possible fate of aryl radicals generated by the fragmentation of the substrate radical anion. As previously outlined, such radicals can undergo three possible reactions: (i) further reduction by electron exchange in solution[17] (reactions 9 and 10), and (ii) hydrogen atom abstraction from the solvent (SH) followed by the reduction[18] of the radical $S^{\bullet}$, reactions 6 and 7, and (iii) nucleophilic attack as shown in reaction 3. In the first two cases, i.e., with reactions 1 + 2 + 9 and 10 as well as with reactions 1 + 2 + 6 + 7, two electrons would be consumed per mole of starting material, while a zero-electron consumption should be observed in the case of a chain-propagating nucleophilic attack. In the case of **1a** the rate constants for the reduction of 4-cyanophenyl radical via reactions 9 and 10 can be safely taken as k_{diff} (2×10^{10} M^{-1} s^{-1} in ACN)[18] in view of the value of the redox potentials of **1a**/**1a**$^{\bullet-}$ ($E° = -1.19$ V/SCE) and **2a**/**2a**$^{\bullet-}$ ($E° = -2.08$ V/SCE) and of the known reducibility of $Ar^{\bullet}$. As the sum of the concentrations of **1a**$^{\bullet-}$ and **2a**$^{\bullet-}$ cannot exceed that of the initial substrate (1 mM) a maximum approximate value ($k_{\mathrm{red}} = 2 \times 10^7$ s^{-1}) can be estimated for the reduction of $Ar^{\bullet}$. The pseudo-first-order rate constant for hydrogen atom abstraction from acetonitrile by the 4-cyanophenyl radical has already been measured: [19] $k_{\mathrm{H}} = 4 \times 10^7$ s^{-1}. Therefore, the overall rate constant for the two-electron path can be taken as $k_{\mathrm{red}} + k_{\mathrm{H}} = 6 \times 10^7$ s^{-1}. From this value and the observed charge consumption of 0.53 e^- per molecule a value of $k_{\mathrm{Nu}} = 1.7 \times 10^8$ s^{-1} can be calculated for the pseudo-first-order rate constant of nucleophilic attack of benzenethiolate on the 4-cyanophenyl radical at 25 °C. Hence, taking $[Nu^-] =$ 1 mM as an upper limit, a lower limit of 1.7×10^{11} M^{-1} s^{-1} can be approximately[20] assumed for the relevant second-order rate constant, a value which is clearly higher than diffusion, suggesting that most aryl radicals are effectively cage-trapped by the benzenethiolate anion. Examination of Table I shows that peak Ic corresponds to a consumption of electricity which is always lower than 1 e^- per molecule indicating the generality of the phenomenon under investigation. On these grounds the conceivable intermediacy of aryldiazenyl radicals along the $\mathbf{1}^{\bullet-}$ fragmentation path can be confidently disregarded; actually, the estimated[21] rates of nitrogen expulsion from $ArN_2^{\bullet}$ are some order of magnitude lower than diffusion, thus allowing escape from the cage of any formed diazenyl radical.

A classical way of probing the incidence of cage processes is represented by the variation of the viscosity of the medium, a parameter which has been shown[12] to increase the cage effect: this should favor, in our case, the coupling between the 4-cyanophenyl radical and benzenethiolate, with a consequent decrease in peak Ic. Actually, the experimental data of Table II must herein be discussed on the basis of additional parameters such as, e.g., the H atom donating ability of the solvent itself (reaction 6), the solvation of reagents and/or products, and the possibility of different termination processes involving the aryl radical. The relative influence of such parameters would be somewhat difficult to forecast within the $S_{RN}1$ frame even in the absence of a cage effect; for example, although ACN is a 2.3-fold better hydrogen atom donor than DMSO, higher yields of $S_{RN}1$ products have been sometimes observed in ACN than in DMSO.[22] If one considers the results obtained on glassy carbon (Table II), PhCN appears as a rather good solvent but not as good as could be expected on the grounds of its almost negligible hydrogen donating ability.[22] With this solvent, a homolytic aromatic substitution can take place (by the 4-cyanophenyl radical on the solvent) whose rate constant is of the same order of magnitude as the hydrogen atom abstraction.[24] DMSO, which is more viscous and a somewhat poorer H-atom donor than ACN, should give a higher substitution efficiency; actually, this is not observed possibly as a consequence of solvation effects. On the other hand, DMF, whose viscosity is intermediate between those of ACN and DMSO, but which is a 14-fold better H-atom donor than DMSO, results in turn to be a less suitable solvent for the $S_{RN}1$ process. Thus, the results obtained through changes of solvents do not clearly point to a correlation between the viscosity and the substitution efficiency but, at least, they show that the low value for the height of peak Ic is by no means casual.

Experiments aimed at trapping the species involved represent an alternative tool to verify the existence of a cage reaction. For this purpose we have tested the effect of an "external" nucleophile, choosing the cyanide ion for the reasons outlined in the previous section. The addition of increasing amounts of cyanide while recording the cyclic voltammogram of **1a** makes the peak of terephthalonitrile **4** appear and from its height the percentage (A) of **1a** which has been transformed into **4** through an $S_{RN}1$ reaction can be obtained. At the same time peak Ic decreases; its height is related to the fraction (B) of

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(17) (a) Amatore, C.; Chaussard, J.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012. (b) In the case of azo sulfides, due to its relatively slow cleavage, the radical anion has time to diffuse away from the electrode before fragmenting; the neutral radical is thus produced in the solution and would be reduced by homogeneous electron transfer than by heterogeneous electron transfer at the electrode.[17a] This can be put on a quantitative basis by calculating the parameter log p: its value of 1.45 shows that the system is under a DISP control.[17a]

(18) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

(19) M'Halla, F.; Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120.

(20) In the preceding estimation we have clearly overestimated the rate of solution reduction by taking the concentration of **1a**$^{\bullet-}$ and **2a**$^{\bullet-}$ as 1 mM, but even if such a reduction was negligible the gross conclusions would not be much affected.

(21) Brede, O.; Menhert, R.; Naumann, W.; Becker, H. G. O. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 666.

(22) Bunnett, J. F.; Scamehorn, R. G.; Traber, P. *J. Org. Chem.* **1976**, *41*, 3677. (b) Degrand, C.; Prest, R.; Compagnon, P. L. In *Electroorganic synthesis, Festschrift for Manuel Baizer*; Little, R. D., Weinberg, N. L., Eds.; Marcel Dekker: New York, 1991; p 45.

(23) (a) The bond dissociation energy of the aromatic C–H bond is 460 kJ/mol compared with the value of 389 kJ/mol for the $H{-}CH_2CN$ bond.[23b] Furthermore, it was shown by Russell[15a] that addition of an aromatic compound in the RH/CCl_4 solvent does not change the C_6H_6/C_6H_5Cl ratio obtained from the decomposition of (phenylazo)triphenylmethane. (b) *Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca-Raton, 1983.

(24) (a) The rate constant for the attack of the phenyl radical on benzene[24b] is $k = 10.3 \times 10^5$ M^{-1} s^{-1}, while that for hydrogen atom abstraction[15a,24b] by the same radical from ACN is $k_{\mathrm{H}} = 5.22 \times 10^5$ M^{-1} s^{-1}. (b) Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589.

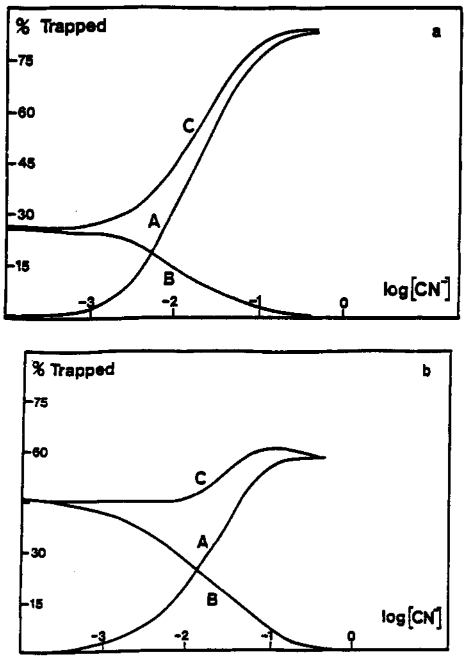


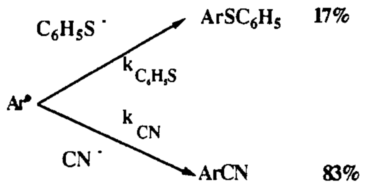
Figure 3. Trapping by CN$^-$ of 4-cyanophenyl radicals produced by reduction of **1a** (a) in ACN and (b) in DMSO: (A) fraction trapped by CN$^-$; (B) fraction trapped by the solvent or reduced; (C) sum of A and B.

4-cyanophenyl radical trapped by the solvent or reduced to the carbanion, both reactions consuming 2 e$^-$ per molecule. The fractions A and B, as well as their sum C, are plotted in Figure 3 against log [CN$^-$]. The complement 100 − C represents the portion of the aryl radical reacting with benzenethiolate to give **2a**, either in the cage or outside the cage. Anyway, we can confidently neglect the percentage of **2a** formed outside the cage as the concentration of benzenethiolate in the bulk solution cannot exceed 1 mM (the initial concentration of **1a**) and, as reported in the Results a 1 mM concentration of benzenethiolate does not lead to any significant reaction with 4-cyanophenyl radicals deriving from a 1 mM solution of 4-bromobenzonitrile. Therefore, at the highest CN$^-$ concentration, C represents the total percentage of radicals trapped by cyanide ions in the solution and 100 − C must represent the percentage of these radicals reacting with benzenethiolate in the solvent cage.[25]

The curves of Figure 3 can be discussed in the light of the analysis developed by Noyes.[12,26] Once the radical anion **1a**$^{\bullet-}$ fragments to 4-cyanophenyl radical and benzenethiolate, these two species may undergo primary recombination in the cage in which they are formed before being separated by as much as a molecular diameter. If the fragments escape the cage, they initially undergo a random diffusive displacement of the order of a molecular diameter; during this random diffusion the fragments from a specific displacement may reencounter each other and undergo a secondary recombination. If the fragments escape both the primary and secondary recombination, the 4-cyanophenyl radical will react either with the "external" nucleophile or with the solvent or will be reduced. Curve C of Figure 3 is in agreement with the curve representing Noyes' predictions. The initial flat region mirrors a situation where all free radicals (i.e., those having escaped both primary and secondary recombinations) are engaged in the cited two-electron termination processes. This is followed by a rising portion featuring the effect of the "external" nucleophile, which gradually scavenges both free radicals (thus replacing the two-electron terminations with a zero-electron S$_{RN}$1 cycle) and secondary pairs (thus lowering the yield of **2a**, as also evidenced by the decrease of peak IIc). The plateau at high [CN$^-$], is indicative of the complete depletion of secondary pairs, showing that even at the largest CN$^-$ concentrations there remains a fraction of aryl radicals (17% in ACN and 43% in DMSO) which react with the "internal" nucleophile PhS$^-$. This complies with the fact that primary pairs cannot be trapped as confirmed by the non-zero limit (0.13 e$^-$ per molecule in ACN and 0.28 in DMSO[27]) observed (Figure 2, curve c) for the height of the reduction peak of **2a** (IIc).

It is interesting to note that although, as discussed above, the S$_{RN}$1 process leading to the diaryl sulfide is more efficient in ACN than DMSO (Table II), at high concentration of cyanide (where the fraction of radicals trapped by the solvent or reduced in solution becomes negligible) one can observe (Figure 3) that the more viscous DMSO (24.7 mp) leads to a higher percentage of cage recombination than ACN (3.75 mp) indicating that the effect of viscosity predominates over a solvation effect.

An estimate of the kinetic parameters can be attained when considering that at high [CN$^-$] only two reactions remain in competition for the 4-cyanophenyl radical: the coupling either with PhS$^-$ or with CN$^-$. Thus in ACN:



From there:

$$\frac{k_{C_6H_5S^-}}{k_{CN^-}} \times \frac{[C_6H_5S^-]}{[CN^-]} = \frac{17}{83} \qquad (12)$$

An upper estimate of the concentration of PhS$^-$ can be taken as 1 mM (i.e., the initial concentration of the substrate); the value of $k_{(CN^-)}$ has been measured[16] in liquid ammonia at −40 °C [$k_{(CN^-)} = 3.1 \times 10^7$ M^{-1} s^{-1}], and at 20 °C one can estimate $k_{(CN^-)} = 2 \times 10^9$ M^{-1} s^{-1}. Using such a value in eq 12 one obtains $k_{(C_6H_5S^-)} = 1.3 \times 10^{11}$ M^{-1} s^{-1} in ACN and $k_{(C_6H_5S^-)} = 2.6 \times 10^{11}$ M^{-1} s^{-1} in DMSO. These values are in fair agreement with the estimation (1.7 × 10^{11} M^{-1} s^{-1}) previously obtained on the grounds of a different competition at the level of the aryl radical and give further support to the existence of a cage effect.

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[25] The yields of **4** obtained by cyclic voltammetry (83% in ACN and 57% in DMSO) and by electrolysis (80% in ACN and 64% in DMSO) at high cyanide concentration are in fair agreement. There is, however, a difference in the yields of 4-cyanophenyl phenyl sulfide (**2a**): 17% in ACN and 43% in DMSO by cyclic voltammetry and 8.5% in ACN and 13% by electrolysis. This is likely due to the difference of time scale between both methods; on the longer times of the electrolysis the radical anion **2a**$^{\bullet-}$ is probably not very stable especially in DMSO, leading to **3a** and finally to benzonitrile. In the presence of cyanide, in addition to the chain reaction which yields **2a**$^{\bullet-}$ and then **2a**, an endergonic electron exchange can take place between **4**$^{\bullet-}$ and **2a** leading also to **2a**$^{\bullet-}$, the equilibrium being displaced by decomposition of **2a**$^{\bullet-}$.

[26] (a) Noyes, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2042. (b) Noyes, R. M. *J. Am. Chem. Soc.* **1956**, *78*, 5846. (c) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129.

[27] This number corresponds to sum of the yields of **2a** (14%) and **3** (14%) as we have shown above that **3a** is product obtained through a further reaction of **2a**.

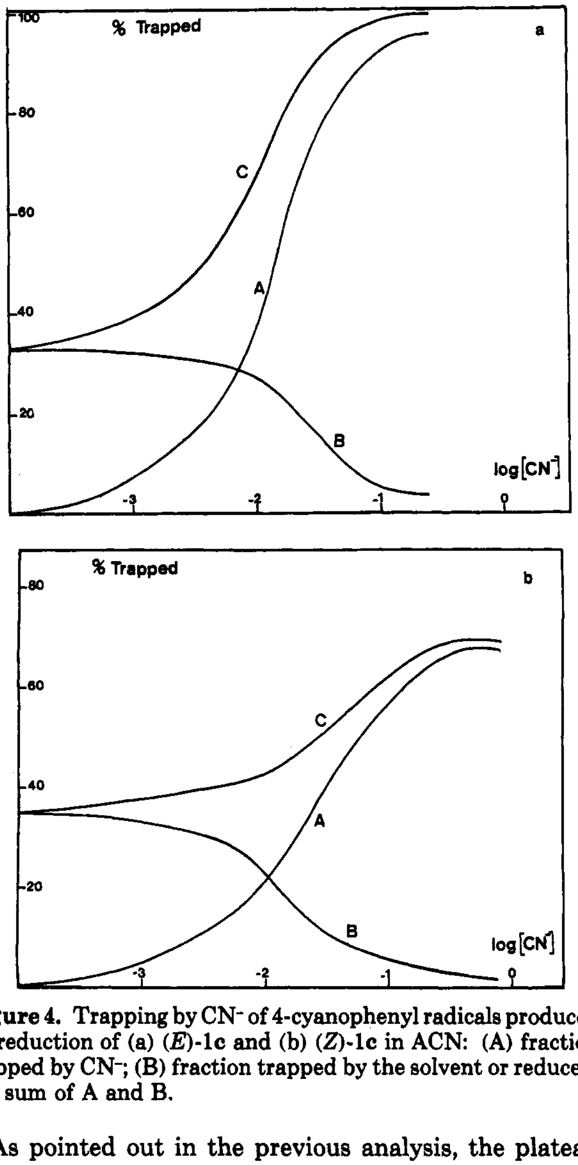

Figure 4. Trapping by CN^- of 4-cyanophenyl radicals produced by reduction of (a) (*E*)-**1c** and (b) (*Z*)-**1c** in ACN: (A) fraction trapped by CN^-; (B) fraction trapped by the solvent or reduced; (C) sum of A and B.

As pointed out in the previous analysis, the plateau observed at high CN^- concentrations could reflect the presence of primary pairs which cannot be trapped by an "external" nucleophile. However, the two reactive fragments herein ($Ar^\bullet$ and RS^-) are somewhat more far away than theorized by Noyes for primary pairs,[26] due to the nitrogen molecule which is bound to separate them during their formation in reaction 2. Thus, one can speculate that the fraction of **2** that is not suppressed by addition of CN^- would rather derive from a concerted reaction at the level of the radical anion $1^{\bullet-}$ leading to the explusion of N_2. An additional hint at this regard could be envisaged in occurrence that trapping of the same 4-cyanophenyl radicals by CN^-, the "external" nucleophile, is more efficient (Figure 4) starting from the (*E*)-(4-cyanophenyl)-azo *tert*-butyl sulfide [(*E*)-**1c**] (96% of trapping) than starting from the (*Z*)-isomer (65% of trapping) although these two isomers present the same cyclic voltammetry.

These results can be rationalized in the following way: the radical anion of the (*E*)-isomer fragments to give the 4-cyanophenyl radical which could recombine in the cage with the *tert*-butanethiolate anion or could be trapped outside of the cage by the cyanide nucleophile, while the radical anion of the (*Z*)-isomer would undergo, in competition with the cleavage, the formation of the phenyl carbon–sulfur bond concertedly with the cleavage of the phenyl carbon–nitrogen and sulfur–nitrogen bonds. This concerted reaction would not be possible for stereochemical reasons with the (*E*)-isomer.[28] As suggested by a reviewer, an alternative explanation of the results of Figure 4 would take into account the fact that the fragmentation of $1c^{\bullet-}$ is bound to leave $Ar^\bullet$ and RS^- separated by a nitrogen molecule for the (*E*)-isomer, but much aside (and thus ready for in-cage coupling) for the (*Z*)-isomer.

Conclusion

Besides the synthetic interest of processes initiated by their one-electron reduction, aryl azo sulfides permit us to unveil some new aspects of $S_{RN}1$ reactions. The main actors of the reaction herein ($Ar^\bullet$ and RS^-) stem from the same molecule, and one observes a very effective recombination of these two species. For substrates **1a**, **1b**, and (*E*)-**1c**, all characterized by a trans configuration around the N=N double bond, trapping experiments strongly support an in-cage coupling between $Ar^\bullet$ and RS^- after fragmentation of the relevant radical anions: the results of such experiments nicely fit Noyes' prediction,[26] which dates back to the 1960s and has been verified only once before.[12,29] Moreover, some hints and a comparison of the behavior of (*E*)-**1c** and (*Z*)-**1c** could also suggest some competitive concerted formation of $ArSR^{\bullet-}$ from $ArN{=}NSR^{\bullet-}$, with N_2 extrusion, particularly for the cis substrate (*Z*)-**1c**.

Recently, the occurrence of the $S_{RN}1$ mechanism has been challenged,[30] and an $S_{RN}2$ mechanism has been claimed to be responsible for the observed chain transformation of $ArX^{\bullet-}$ (where X is a leaving group) into $ArNu^{\bullet-}$ in the presence of a nucleophile Nu^-. In the case of azo sulfides an $S_{RN}2$ mechanism should be written as follows:

$$\text{initiation}\quad 2ArN{=}NSR + 2\,e^- \rightarrow 2ArN{=}NSR^{\bullet-} \qquad (13)$$

$$ArN{=}NSR^{\bullet-} \rightarrow Ar^\bullet + N_2 + {}^-SR \qquad (14)$$

$$\text{propagation}\quad ArN{=}NSR^{\bullet-} + {}^-SR \rightarrow ArSR^{\bullet-} + N_2 + {}^-SR \qquad (15)$$

$$ArSR^{\bullet-} + ArN{=}NSR \rightarrow ArSR + ArN{=}NSR^{\bullet-} \qquad (16)$$

In the presence of an "external" nucleophile two further reactions should be added:

$$ArN{=}NSR^{\bullet-} + CN^- \rightarrow ArCN^{\bullet-} + N_2 + {}^-SR \qquad (17)$$

$$ArCN^{\bullet-} + ArN{=}NSR \rightarrow ArCN + ArN{=}NSR^{\bullet-} \qquad (18)$$

With such a mechanism, the thiolate nucleophile is produced in the propagation cycle by decomposition of one azo sulfide radical anion and, in the next step, attacks

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(28) The different behaviors observed between (*E*)-**1c** and (*Z*)-**1c** also show that the rotation around the —N=N— bond does not have time to take place before the cleavage of the radical anion. Would such a rotation occur, identical results should be observed for both isomers. The same results are also in agreement with the nonintermediacy of $ArN_2^\bullet$ in the reactions.

(29) (a) Wu, C. H. S.; Hammond, G. S.; Wright, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 5386. (b) Hammond, G. S.; Wu, C. H. S.; Trapp, O. D.; Warkentin, J.; Keys, R. T. *J. Am. Chem. Soc.* **1960**, *82*, 5394. (c) Waits, H. P.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 1911. (d) Fox, J. R.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 1918.

(30) Denney, D. B.; Denney, D. Z. *Tetrahedron* **1991**, *47*, 6577.

another azo sulfide radical anion. Under such conditions, where the thiolate behaves as an "external" nucleophile, it is difficult to see why it should be such a good nucleophile. Furthermore, with such a mechanism, one should not observe a plateau (Figures 3 and 4) but rather a continuous increase of the yield of ArCN for larger and larger concentrations of CN^-. Finally an $S_{RN}2$ mechanism could not rationalize the difference in behavior between (*E*)- and (*Z*)-**1c**.

Experimental Section

For cyclic voltammetry we used a home-built potentiostat[31] equipped with a positive feedback ohmic drop compensation device and a Tacussel GSTP4 signal generator. The electrode was a glassy carbon disk (Tokai Corp.) of 3-mm diameter or a mercury drop hanging from a 1-mm gold disc. The reference electrode was a saturated calomel electrode separated from the solution by a salt bridge. For fast cyclic voltammetry a 17-μm gold electrode was used along with a specially designed potentiostat,[32] a Schlumberger signal generator, and a fast digital acquisition oscilloscope Nicolet 4180.

Solvents supporting electrolytes and tetraethylammonium cyanide were of analytical quality. Azo sulfides[4c] **1a** and **1b** and the sulfides **2a**, **2b**,[4c] and **3**[33] were synthesized along known procedures.

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[33] Evans, T. L.; Kinnard, R. D. *J. Org. Chem.* **1983**, *48*, 2496.