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Regioselective Bond Cleavage in the Dissociative Electron Transfer to Benzyl Thiocyanates: The Role of Radical/Ion Pair Formation

Emad M. Hamed, Hanh Doai, Christopher K. McLaughlin, and Abdelaziz Houmam*

Contribution from the Electrochemical Technology Center, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Received September 30, 2005; E-mail: houmam@chembio.uoguelph.ca

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Abstract: Important aspects of the electrochemical reduction of a series of substituted benzyl thiocyanates were investigated. A striking change in the reductive cleavage mechanism as a function of the substituent on the aryl ring of the benzyl thiocyanate was observed, and more importantly, a regioselective bond cleavage was encountered. A reductive α-cleavage (CH_2-S bond) was seen for cyano and nitro-substituted benzyl thiocyanates leading to the formation of the corresponding nitro-substituted dibenzyls. With other substituents (CH_3O, CH_3, H, Cl, and F), both the α (CH_2-S) and the β (S−CN) bonds could be cleaved as a result of an electrochemical reduction leading to the formation of the corresponding substituted monosulfides, disulfides, and toluenes. These final products are generated through either a protonation or a nucleophilic reaction of the two-electron reduction-produced anion on the parent molecule. The dissociative electron transfer theory and its extension to the formation/dissociation of radical anions, as well as its extension to the case of strong in-cage interactions between the produced fragments ("sticky" dissociative electron transfer (ET)), along with the theoretical calculation results helped rationalize (i) the observed change in the ET mechanism, (ii) the dissociation of the radical anion intermediates formed during the electrochemical reduction of the nitro-substituted benzyl thiocyanates, and more importantly (iii) the regioselective reductive bond cleavage.

Introduction

Since the introduction of the dissociative electron transfer (ET) theory,[1] much attention has been given to understanding whether ET and bond breaking are concerted or successive steps and to factors controlling the occurrence of either mechanism.[2] For a stepwise mechanism, the Hush−Marcus model,[3] of outersphere electron transfer, can be applied to the electron transfer step. On the other hand, when the ET and the bond breaking occur in a concerted manner, a model based on the Morse curve picture of bond breaking is used.[1] For both mechanisms, the reaction activation energy depends on both thermodynamic and kinetic factors, through a quadratic activation-driving force relationship (eq 1).

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta G^{\circ}}{4\Delta G_0^{\ddagger}}\right)^2 \qquad (1)$$

The only difference is the contribution, for a concerted ET mechanism, of the bond dissociation energy (BDE) of the fragmented bond to the activation barrier, $\Delta G_0^{\ddagger}$, which involves only the solvent (λ_0) and the inner (λ_i) reorganization energies for a stepwise mechanism (eq 2). $\Delta G^{\ddagger}$ (the activation free energy), ΔG° (the reaction free energy), and $\Delta G_{0,s}^{\ddagger}$ and $\Delta G_{0,c}^{\ddagger}$ (i.e., the activation energy at zero driving force) represent the intrinsic barriers for a stepwise and a concerted ET, respectively.

$$\Delta G_{0,s}^{\ddagger} = \frac{\lambda_i + \lambda_0}{4} \text{ and } \Delta G_{0,c}^{\ddagger} = \frac{\lambda_0 + \mathrm{BDE}_{R-X}}{4} \qquad (2)$$

The difference in the reaction free energy between the two ET mechanisms can be expressed by the corresponding standard potentials (eq 3).

$$E^0_{RX/RX^{\bullet-}} - E^0_{RX/R^{\bullet}+X^-} = E^0_{RX/RX^{\bullet-}} + D_{R-X} - E^0_{X^{\bullet}/X^-} - T\Delta S_{RX/R^{\bullet}+X^{\bullet}} \qquad (3)$$

The weaker the bond and the more positive the $E^0_{X^{\bullet}/X^-}$, the more favorable the thermodynamics of the concerted mechanism are.

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[3] See, for example: (a) Marcus, R. A. *J. Chem. Phys*. **1955**, *24*, 4955. (b) Marcus, R. A. *J. Chem. Phys*. **1956**, *24*, 966. (c) Marcus, R. A. *J. Chem. Phys*. **1956**, *24*, 979. (d) Hush, N. S. *J. Chem. Phys*. **1958**, *28*, 962. (e) Hush, N. S. *Trans. Faraday Soc*. **1961**, *57*, 557. (f) Marcus, R. A. *Annu. Rev. Phys. Chem*. **1964**, *15*, 155. (g) Marcus, R. A. *J. Chem. Phys*. **1965**, *43*, 679. (h) Marcus, R. A. Theory and Applications of Electron Transfers at Electrodes and in Solution. In *Special Topics in Electrochemistry*; Rock, P. A., Ed.; Elsevier: New York, 1977; pp 161−179. (i) Marcus, R. A. *Faraday Discuss. Chem*. **1982**, *74*, 7. (j) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

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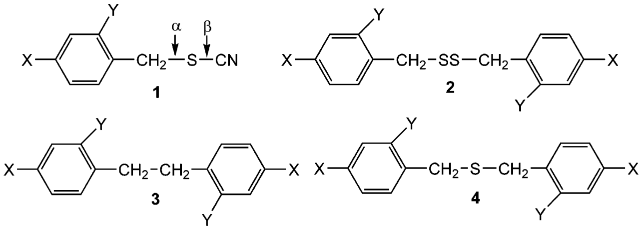
In cyclic voltammetry (CV), the peak characteristics can be used efficiently to obtain accurate mechanistic, kinetic, and thermodynamic data by application of the adequate theory. When the single ET product cannot be detected experimentally (high scan rate[4] and homogeneous catalysis[4,5]), the transfer coefficient (α), which is directly related to the intrinsic barrier (eq 4), is a sensitive probe of the mechanistic nature of the first electron transfer in dissociative processes. The transfer coefficient can be determined from the electrochemical peak characteristics (peak width, $E_p - E_{p/2}$)[6a] or from the variation of the peak potential, E_p, with the scan rate, v.[6b] In a concerted mechanism, a value significantly lower than 0.5 is expected, whereas an α value close to or higher than 0.5 is expected in the case of a stepwise mechanism.[7]

$$\alpha = \frac{\partial \Delta G^{\ddagger}}{\partial \Delta G^{0}} = \frac{1}{2}\left(1 + \frac{\Delta G^{0}}{4\Delta G_{0}^{\ddagger}}\right) \qquad (4)$$

The dissociative ET model has been successfully tested for a number of types of organic compounds.[1,2,8] Equation 4 predicts a linear variation of α with the driving force; however, a few experimental systems have shown a nonlinear variation.[9] This is an indication of a transition between concerted and stepwise mechanisms as a function of the driving force which could easily be controlled in electrochemistry by varying the electrode potential. This behavior demonstrates that the nature of the ET process is not merely dictated by the existence of an intermediate radical anion but rather by the energetic advantage of one process over another.

The dissociative ET has also been successfully used to describe the formation/dissociation reactions of radical ions.[1b,2,10] More recently, this theory has been extended to describe dissociative ET reactions involving strong interactions between the produced fragments (sticky dissociative ET).[11] The intermediate formation of radical/ion pairs during the concerted reductive cleavage of carbon tetrachloride,[11a,b] 4-cyanobenzyl chloride,[11b] and haloacetonitriles[11c] had been shown to affect both the mechanism and the rate of these ET processes. The strength of these interactions has been shown to depend on the Lewis acid–base properties of the involved fragments as well as on the nature of the used solvent as expected.[11]

Chart 1



Y = H; X = CH_3O (**a**) ; CH_3 (**b**); H (**c**); Cl (**d**); F (**e**); CN (**f**), NO_2 (**g**) and Y = NO_2; X = H (**h**)

In most reported studies, however, the same bond (R–X) is broken when the ET driving force is changed for a series of compounds.[1,2,8] Although regioselective bond cleavage in dissociative ET reactions has been reported, concrete examples are however limited and the factors controlling the regioselectivity remain unclear.[12] The advances made in the dissociative ET theory may provide the necessary tools to rationalize such a phenomenon and to understand the factors controlling it.

We previously reported the electrochemistry of a series of aryl thiocyanates and showed that their reduction results in the cleavage of the S–CN bond (*β*-cleavage) and involves a unique autocatalytic process.[9a] More recently, we reported an example of regioselective bond cleavage in the electrochemical reduction of benzyl and *p*-nitrobenzyl thiocyanates.[13] This manuscript describes the full investigation of a series of substituted benzyl thiocyanates **1a–h** (Chart 1). Not only is a change of the ET mechanism observed but also, more interestingly, a clear-cut example of a regioselective bond cleavage is encountered. The factors controlling both the ET mechanism variation and the regioselective bond cleavage are discussed on the basis of the dissociative ET theory, with and without the intermediate formation of radical/ion pairs, and its extension to the formation/dissociation reactions of radical ions[1b,2,10] with the help of theoretical calculations.

Results and Discussion

Voltammetric Behavior and Electrolysis Results. The electrochemical reduction of substituted benzyl thiocyanates (**1a–h**) and their corresponding disulfides (**2a–e**) or substituted dibenzyls (**3f–h**) was studied by cyclic voltammetry (CV) in acetonitrile (CH_3CN), in the presence of tetrabutylammonium tetrafluoroborate (TBAF, 0.1 M) at a glassy carbon electrode.

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(6) (a) $\alpha = (RT/F)(1.85/E_{p/2} - E_p)$. (b) $\partial E_p/\partial \log v = -29.5/\alpha$ at 20 °C.

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Table 1. Electrochemical Characteristics of Substituted Benzyl Thiocyanates **1a**−**h**

$ArCH_2SCN$	E_{p1}[a] (V vs SCE)	n[b]	E_p–log(v) slope[c]	α[d]	E_p–$E_{p/2}$ (mV)	α[e]	E_{p2}[f] (V vs SCE)
1a	−2.20	1.04	−85	0.35	160	0.29	−2.43
1b	−2.10	1.02	−107	0.27	189	0.25	−2.50
1c	−2.08	1.2	−98	0.30	154	0.30	−2.37
1d	−1.96	0.89	−92	0.32	167	0.28	−2.17
1e	−2.18	1.19	−103	0.28	187	0.25	−2.25
1f	−1.72	0.99	−88	0.34	124	0.37	−2.72
1g	−0.89	0.90	−48	0.61	79	0.60	−1.17
1h	−0.90	1.04	−50	0.60	67	0.69	−1.18, −1.29

[a] First peak potential. [b] Number of electrons per molecule. [c] In mV/log(v). [d] From E_p vs log(v) curve. [e] From peak width. [f] Second peak potential.

Scheme 1

$$\mathrm{XBnSCN} + e^- \longrightarrow \mathrm{XBn}^\bullet + \mathrm{SCN}^-$$
$$\mathrm{XBn}^\bullet + e^- \longrightarrow \mathrm{XBn}^-$$

Or

$$\mathrm{XBnSCN} + e^- \longrightarrow \mathrm{XBnS}^\bullet + \mathrm{CN}^-$$
$$\mathrm{XBnS}^\bullet + e^- \longrightarrow \mathrm{XBnS}^-$$
$$\mathrm{XBnS}^- + \mathrm{XBnSCN} \longrightarrow \mathrm{XBnSSBnX}$$
$$\mathrm{XBnS}^- + \mathrm{XBnSCN} \longrightarrow \mathrm{XBnSBnX}$$

The peak characteristics (peak potential (E_p), peak width ($E_p-E_{p/2}$), slope of $E_p-\log(v)$, number of electrons per molecule, and transfer coefficient (α) values determined from both peak width and $E_p-\log(v)$ plots) are summarized in Table 1.

Compounds 1a−e. All of these compounds show very similar peak characteristics (Table 1). Their cyclic voltammograms display a first irreversible reduction peak corresponding to the consumption of one electron per molecule (Figure 1a−e). The peak width values are large (from 154 to 189 mV), and the deduced α values (from 0.25 to 0.30) are much lower than 0.5 indicating a reaction kinetically controlled by an irreversible electron transfer step.[1,2] The variation of the peak potentials with the log(v) are all linear with a large slope (from 85 to 107 mV per unit log(v)). The transfer coefficient values determined from the slopes of the $E_p-\log(v)$ plots are in agreement with those obtained from the peak width. In all cases, a second irreversible reduction peak is observed at a lower potential and corresponds to the reduction of the produced substituted dibenzyl disulfide (**2a**−**e**) by comparison with an authentic sample (Figure 1a−e).

The initial ET and the S−CN bond breaking (β-cleavage) are concerted, and the produced thiyl radical is immediately reduced at the electrode yielding the benzyl thiolate anion. The reduction potentials of substituted arylthiyl radicals have already been reported (from 0.5 to −0.1 V vs SCE).[14] As for the aryl thiocyanates, the substituted benzyl thiolate reacts on the parent benzyl thiocyanate (**1a**−**e**) to yield the corresponding disulfide (Scheme 1). Nucleophilic attack by thiolates on both the sulfur and the benzylic carbon of substituted benzylic thiocyanates has been reported previously in the literature.[15] In a control reaction, tetrabutylammonium benzyl thiolate and **1c** were mixed to yield both dibenzyl disulfide (**2c**) and dibenzyl sulfide (**4c**).

Electrolyses of **1a**−**e** (Table 2) confirmed the stoichiometry of one electron per molecule and the formation of the corresponding disulfides (**2a**−**e**) and sulfides (**4a**−**e**). This resulted from attack of the substituted benzyl thiolate (generated through a two-electron β-reductive cleavage) on either the sulfur or the benzylic carbon of **1**, with subsequent ejection of the cyanide anion or the thiocyanate anion, respectively. Furthermore, the electrolyses also showed formation of the corresponding substituted toluenes through an α-reductive cleavage. The yields seem to slightly depend on both the concentration of the initial substrate (which is expected because the generated intermediates react with their parent substrates) and the electrolysis potential.

Table 2. Electrolyses Results of Substituted Benzyl Thiocyanates **1a**−**g**

electrolysis of $ArCH_2SCN$[a]	$(ArCH_2S)_2$: %	$(ArCH_2)_2S$: %	$(ArCH_2)_2$: %	$ArCH_3$: %
1a	**2a**: 77	**4a**: 4		18
1b	**2b**: 52	**4b**: 20		26
1c	**2c**: 61	**4c**: 6		33
1d	**2d**: 64	**4d**: 23		11
1e	**2e**: 76	**4e**: 2		22
1f			**3f**: 97	
1f + PhOH[b]				97
1g			**3g**: 98	
1g + PhOH[b]				98
1h			**3h**: 97	
1h + PhOH[b]				98

[a] In CH_3CN + Me_4NBF_4 (0.1 M) at a glassy carbon electrode. [b] [**1**]/[PhOH] = 1:2.

This result indicates that the reductive cleavage of compounds **1a**−**e** could then involve either an α- or a β-cleavage through Scheme 1.

An important result in the reduction of compounds **1a**−**e** is the absence of autocatalysis, shown by trace crossing in the electrochemical reduction of aryl thiocyanates.[9a] The reason is that the corresponding disulfides (**2a**−**e**) are more difficult to reduce than the corresponding substituted benzyl thiocyanates (**1a**−**e**), and therefore, a second reduction peak is seen at a more negative potential.

Compound 1f. The cyclic voltammetry of *p*-cyanobenzyl thiocyanate (**1f**) displays an irreversible monoelectronic reduction peak at a potential of $E_p = -1.72$ V vs SCE (Figure 1f). The peak width has a value of 124 mV, and the slope of the E_p vs log(v) plot is equal to 88 mV per unit log(v). The deduced transfer coefficient values are 0.34 and 0.37. These peak characteristics are similar to the ones exhibited by compounds **1a**−**e**. The initial electron transfer to **1f** is a concerted process where the ET and the bond cleavage occur simultaneously. The first peak is followed by a second reversible reduction peak ($E° = -2.72$ V vs SCE) corresponding to the reduction of 4,4′-dicyanodibenzyl (**3f**), by comparison with an authentic sample (Figure 1f), formed as a result of a chemical reaction following

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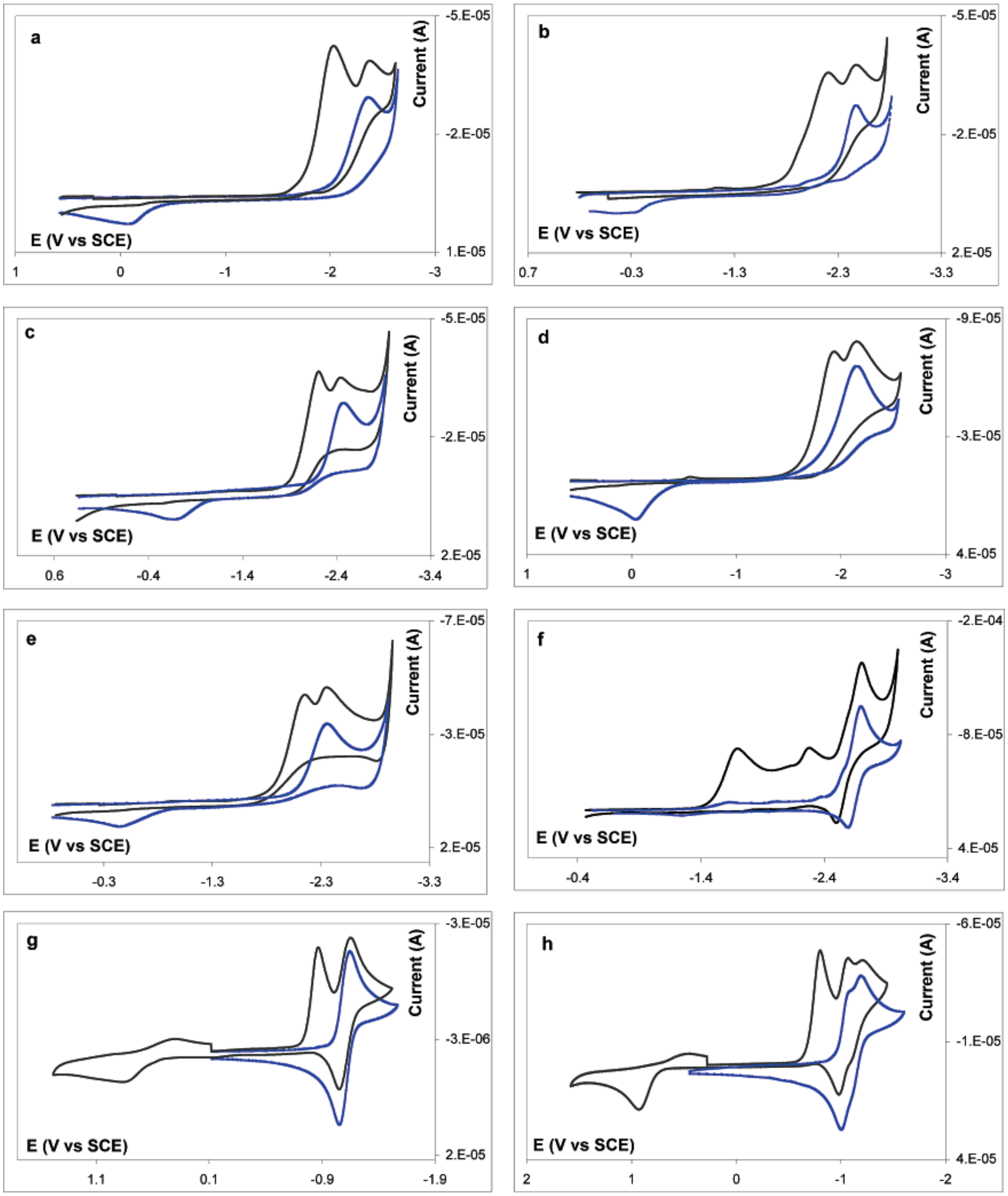

Figure 1. Cyclic voltammetry of CH_3CN/Bu_4NBF_4 (0.1 M) at a glassy carbon electrode at $v = 0.2$ V/s of (a) **1a** (2.61 mM) and **2a** (1.1 mM); (b) **1b** (2.14 mM) and **2b** (1.86); (c) **1c** (2 mM) and **2c** (0.72 mM); (d) **1d** (5 mM) and **2d** (2.93 mM); (e) **1e** (1.86 mM) and **2e** (0.9 mM); (f) **1f** (3.79 mM) and **3f** (1.9 mM); (g) **1g** (2 mM) and **3g** (1.5 mM); and (h) **1h** (2.37 mM) and **3h** (2 mM).

the dissociative ET where the thiocyanate is the leaving group (α-cleavage) and not the cyanide as seen for compounds **1a**−**e**. The electrolysis of **1f** confirmed the stoichiometry of one electron per molecule and yielded the 4,4′-dicyanodibenzyl (**3f**) quantitatively (Table 2). Furthermore, in the presence of excess phenol, the electrolysis of **1f** yields exclusively *p*-cyanotoluene and the stoichiometry increases to two, indicating that **3f** results from a nucleophilic attack of *p*-cyanobenzyl on the starting material **1f** (Scheme 2).

Compounds 1g and 1h. Compounds **1g** and **1h** also show similar CV behavior as a first monoelectronic irreversible peak ($E_p = -0.89$ and -0.90 V vs SCE for **1g** and **1h**, respectively) is observed (Figure 1g,h). The peak width and the slope of the E_p vs log(v) plot are 79 mV and 48 mV/log(v) for **1g** and 67 mV and 50 mV/log(v) for **1h**. These peak characteristics correspond to a stepwise ET involving the intermediacy of a radical anion with a mixed kinetic control by both the ET and the bond dissociation steps. The first irreversible peak is followed by a second reversible peak ($E^0 = -1.17$ V vs SCE) for **1g** and two close reversible waves ($E^0 = -1.18$ V and -1.29 vs SCE) for **1h**, corresponding to the reduction of the resulting

Scheme 2

$$\mathrm{NCBnSCN} + e^- \longrightarrow \mathrm{NCBn}^{\bullet} + \mathrm{SCN}^-$$

$$\mathrm{NCBn}^{\bullet} + e^- \longrightarrow \mathrm{NCBn}^-$$

$$\mathrm{NCBn}^- + \mathrm{NCBnSCN} \longrightarrow \mathrm{NCBnBnCN} + \mathrm{SCN}^-$$

Table 3. Bond Length and Bond Dissociation Energies for the α- and *β*-Bonds for the Substituted Benzyl Thiocyanates **1a**−**h**

	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
$l_{\mathrm{ArCH_2-SCN}}{}^{a}$	1.8851	1.8819	1.8799	1.8797	1.8798	1.8772	1.8761	1.8761
$D_{\mathrm{ArCH_2-SCN}}{}^{b}$	50.62	50.53	50.42	49.45	50.04	47.60	47.01	46.72
$l_{\mathrm{ArCH_2S-CN}}{}^{a}$	1.7006	1.7007	1.7007	1.7007	1.7016	1.7006	1.7006	1.6996
$D_{\mathrm{ArCH_2S-CN}}{}^{b}$	104.01	100.54	100.24	99.81	100.02	98.91	98.54	97.10
ΔD^{b}	53.39	50.01	49.82	50.36	49.98	51.31	51.53	50.38

[a] Bond length in Å. [b] Bond dissociation energy in kcal/mol.

Scheme 3

$$\mathrm{O_2NBnSCN} + e^- \rightleftharpoons \mathrm{O_2NBnSCN}^{\bullet -}$$
$$\mathrm{O_2NBnSCN}^{\bullet -} \longrightarrow \mathrm{O_2NBn}^{\bullet} + \mathrm{SCN}^-$$
$$\mathrm{O_2NBn}^{\bullet} + e^- \longrightarrow \mathrm{O_2NBn}^-$$
$$\mathrm{O_2NBn}^- + \mathbf{2} \longrightarrow \mathrm{O_2NBnBnNO_2} + \mathrm{SCN}^-$$

dibenzyl compounds (4,4′-dinitrodibenzyl (**3g**) and 2,2′-dinitrodibenzyl (**3h**) for **1g** and **1h**, respectively) by comparison with authentic samples (Figure 1g,h), formed as a result of a chemical reaction following an α-cleavage of the radical anion generated by the initial ET in agreement with previous studies.[16] Electrolysis of **1g** and **1h** confirmed the stoichiometry of one electron per molecule and showed the quantitative formation of 4,4′-dinitrodibenzyl and 2,2′-dinitrodibenzyl, respectively, with no isocyanate formation.[17,18] It has been reported that the photoinduced ET to **1g** results in the formation of the corresponding isocyanate through isomerization of the radical anion intermediate.[17,18] Such an isomerization does not seem to take place under electrochemical conditions as the reduction of both compounds yields the thiocyanide anion, of which the oxidation peak can easily be identified (Figure 1g,h) as the potential is scanned back toward positive values. Similar to compound **1f**, in the presence of excess of phenol, the electrolyses of **1g** and **1h** yield exclusively the corresponding substituted toluene (4-nitrotoluene and 2-nitrotoluene, respectively) and the stoichiometry increases to two, indicating that the compounds **3g**,**h** are the result of a nucleophilic attack of the nitrobenzyl anion on the parent substituted benzyl thiocyanate (**1g**,**h**) (Scheme 3).

Theoretical Investigation. To help understand both the difference in the ET mechanism and the regioselective bond cleavage, a theoretical study at the B3LYP level has been performed for all compounds. The study clearly shows that while the LUMOs for compounds **1a**−**f** are spread all over the molecule those for the nitro-substituted benzyl thiocyanates (**1g**,**h**) are more located on the aryl moiety with a lower coefficient on the CH_2SCN group (Figure 2). This suggests that in the latter case the incoming electron is hosted by the π^* of the aryl moiety to provide a radical anion in accordance with a stepwise mechanism as suggested by the electrochemical data. Introduction of a nitro group in **1g**,**h** not only lowers the LUMO energy level but also shifts its location to the aryl moiety. Once the radical anion ($\mathbf{1g,h}^{\bullet -}$) is formed, the electron will be transferred from the π^* to the σ CH_2-S bond.

For compounds **1a**−**f**, the incoming electron would be directly injected into a σ-bond (α or β) simultaneously with its dissociation in a concerted ET mechanism. In the particular case of **1f**, one could notice that even if the LUMO is not localized on the aryl moiety there is certainly less participation of the SCN group compared to compounds **1a**−**e**.

We also calculated the bond dissociation energies (*D*) as well as the bond length (*l*) for both the α- and *β*-bonds for all studied compounds (Table 3). These data show very little variation in both parameters with the nature of the substituent, similar to the case of benzyl halides.[8b] Furthermore, a large difference is observed between the α- and *β*-bond strengths for all compounds, with the *β*-bond being about 50 kcal/mol stronger than the α one. This important difference is expected considering that the α-cleavage would lead to two more stable radicals than the *β*-cleavage. A benzylic radical ($ArCH_2^{\bullet}$) is more stable than a benzyl thiyl radical ($ArCH_2S^{\bullet}$) which is more localized on the sulfur atom. The oxidation potentials of the cyanide and thiocyanide anions, discussed below, also suggest that the thiocyanyl radical is more stable.

Our electrochemical data along with the calculation results can allow us now to rationalize some of the observed processes.

Stepwise vs Concerted ET Mechanisms. The electrochemical data and the calculated LUMOs are in agreement. For compounds **1a**−**f**, an important contribution of the CH_2SCN group to the LUMO is observed. The incoming electron is injected into a σ-bond with its immediate dissociation in a concerted process. No radical anion intermediate is formed. For **1f**, the introduction of the cyano group affects the LUMO as the SCN group participates less, but an important contribution of the CH_2S group is still observed. The ET is concerted with an α-cleavage. For compounds **1g**,**h**, the introduction of a stronger electron-withdrawing group (NO_2) lowers the LUMO energy but more importantly shifts its location. For the two latter compounds (**1g**,**h**), the LUMO is totally localized on the nitroaryl moiety. The incoming electron is injected into the π^* of the aryl moiety to provide a radical anion in accordance with a stepwise mechanism as suggested by the electrochemical data. Once the radical anion ($\mathbf{1g,h}^{\bullet -}$) is formed, the electron will be transferred from the π^* to the σ CH_2-S bond (α-cleavage) in a heterolytic mode.[1b,2,10] This difference in the ET mechanism is in agreement with what has been reported earlier for benzyl halides.[8b,19] Besides the proximity of the α-bond to the aryl

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(16) (a) Hlavatý, J. *Collect. Czech. Chem. Commun.* **1983**, *50*, 33. (b) Bartak, D. U.; Shields, T. M.; Hawley, M. D. *J. Electroanal. Chem.* **1971**, *300*, 289.

(17) (a) Isomerization of thiocyanates to the corresponding isocyanates has been observed.[18] In the photoassisted ET to benzyl thiocyanates, the isomerization is believed to result from a recombination of the benzyl radical and the thiocyanide anion through the N atom.[18a] The absence of isocyanate in our case is in agreement with a further reduction of the *p*-nitrobenzyl radical for which one can readily estimate the standard reduction potential ($E^0_{\mathrm{O_2NBn^{\bullet}/O_2NBn^-}} = -0.45$ V vs SCE) using data for related radicals.[17b] (b) Sim, B. A.; Griller, M. D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635.

(18) (a) Wakamatsu, K.; Dairiki, J.; Etoh, T.; Yamamato, H.; Yamamato, S.; Shigetom, Y. *Tetrahedron Lett.* **2000**, *41*, 365. (b) Kotani, M.; Shigetomi, Y.; Imada, M.; Oki, M.; Nagaoka, M. *Heteroatom Chem.* **1997**, *8*, 35. (c) Suzuki, H.; Usuki, M.; Hanafusa, T. *Bull. Chem. Jpn.* **1979**, *52*, 836. (d) Parks, T. E.; Spurlock, A. *J. Org. Chem.* **1973**, *38*, 3922 and references therein.

(19) (a) Lawless, J. G.; Bartak, D. E.; Hawley, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 7121 (b) Bartak, D. E.; Hawley, M. D. *J. Am. Chem. Soc.* **1972**, *94*, 6401. (c) Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1981**, *103*, 103. (d) Koch, D. A.; Henne, B. J.; Bartak, D. E. *J. Electrochem. Soc.* **1987**, *134*, 3062. (e) Jensen, H.; Daasbjerg, K. *Acta Chem. Scand.* **1998**, *52*, 1151.

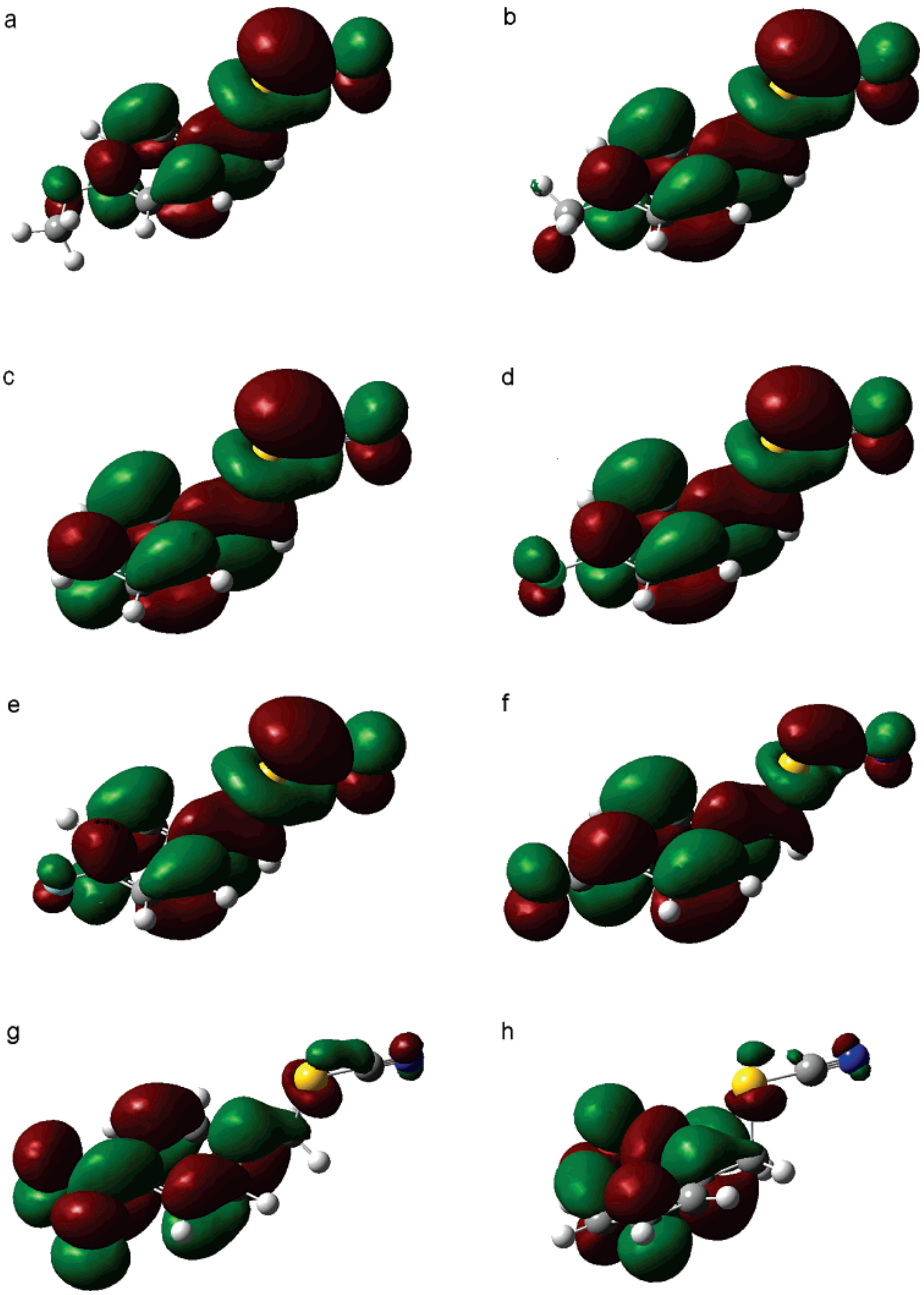

Figure 2. LUMOs of (a) **1a**; (b) **1b**; (c) **1c**; (d) **1d**; (e) **1e**; (f) **1f**; (g) **1g**; and (h) **1h**.

moiety, both the kinetics and the thermodynamics are in favor of an α-cleavage in the case of these two compounds, as discussed below.

Decomposition of 1g,h$^{\bullet-}$. For compounds **1g**,**h**, the decomposition of the radical anion intermediates (**1g**,**h**$^{\bullet-}$) can be understood by considering the extension of the dissociative ET to the decomposition of radical anions.[1b,2,10]

According to this theory, the thermodynamics of the intramolecular heterolytic ET could be described by eq 5:

$$\Delta G^\circ = E - E^0_{\mathrm{RX/R^\bullet + X^-}} = E + D_{\mathrm{R-X}} - E^0_{\mathrm{X^\bullet/X^-}} - T\Delta S_{\mathrm{RX/R^\bullet + X^\bullet}} \quad (5)$$

E is the electrode potential, $E^0_{\mathrm{RX/R^\bullet + X^-}}$ is the standard potential of the RX/R$^\bullet$+X$^-$ couple, $D_{\mathrm{R-X}}$ is the bond dissociation energy of the cleaved bond, $E^0_{\mathrm{X^\bullet/X^-}}$ is the standard potential of the X$^\bullet$/X$^-$ couple, and $\Delta S_{\mathrm{RX/R^\bullet + X^\bullet}}$ is the entropy of the homolytic dissociation reaction.

Knowing the bond dissociation energies for the two bonds (α and β) and the oxidation potential of the leaving group (CN$^-$ for a β-cleavage and NCS$^-$ for an α-cleavage), we can compare the thermodynamics of the two processes. The standard oxidation potential of cyanide in acetonitrile has been previously estimated ($E^0_{\mathrm{CN^\bullet/CN^-}}$ = 2.25 V/SCE[20]), and that of thiocyanide has been determined using CV ($E^0_{\mathrm{NCS^\bullet/NCS^-}}$ = 0.65 V/SCE[19]). Although the big difference (1.6 V) between the oxidation potentials of the two leaving groups clearly favors a β-cleavage,

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(20) $E^0_{\mathrm{CN^\bullet/CN^-}}$ = 2.25 V vs SCE[2g] and $E^0_{\mathrm{NCS^\bullet/NCS^-}}$ = 0.65 V vs SCE as determined by cyclic voltammetry.

this advantage is totally compensated by the huge difference between the bond dissociation energies (≅50 kcal/mol or 2.16 eV) favoring rather an α-cleavage. These data show that from a thermodynamic point of view the α-cleavage is more favorable than the β one.

From a kinetic point of view, the intrinsic barrier for the decomposition of **1g**,**h**$^{\bullet-}$ involves the dissociation energy of the cleaved bond at the level of the radical anion **1g**,**h**$^{\bullet-}$. With the π^* orbital of the aryl moiety being the electron-hospitable orbital in the reduction of **1g**,**h**, the dissociation follows a heterolytic[1b,2,10] cleavage and the contribution of the bond dissociation to the intrinsic barrier of the decomposition of **1g**,**h**$^{\bullet-}$ is described by eq 6. This result shows a total independence on the leaving group's oxidation potential (the only factor that would favor the β-cleavage over the α one). $E^0_{\mathrm{O_2NBn^\bullet/(O_2NBn^\bullet)^{\bullet-}}}$ and $E^0_{\mathrm{O_2NBnS^\bullet/(O_2NBnS^\bullet)^{\bullet-}}}$ would not be very different because they both represent the injection of one electron in the π^* orbital of the nitro phenyl moiety. As well, the solvent reorganization energy would not be very different for the two dissociation modes (α and β).[1b,2,10] If they were, the solvation reorganization energy would be expected to be slightly larger for the β-cleavage because it leads to a smaller anion ($\mathrm{CN^-}$). In this case, the bond dissociation energy, which is in favor of an α-cleavage, is the predominant factor.[21]

$$\Delta G^{\neq}_{0,\mathrm{RX^{\bullet-}/R^\bullet+X^-}} = \frac{1}{4}\left(D_{\mathrm{R-X}} + E^0_{\mathrm{RX/RX^{\bullet-}}} - E^0_{\mathrm{R^\bullet/(R^\bullet)^{\bullet-}}} + T\Delta\bar{S}_{\mathrm{RX^{\bullet-}/R^\bullet+X^-}}\right) + \frac{\lambda_0}{4} \quad (6)$$

It appears that the α-decomposition of **1g**,**h**$^{\bullet-}$ is favored (over the β one) from both a thermodynamic and a kinetic point of view.

Cleavage of the α and *β* Bond for 1a−f. Although the difference in the ET transfer mechanism can readily be understood on the basis of these considerations, it is more difficult to rationalize the regioselective bond cleavage for compounds **1a**−**e** using the "classical" dissociative ET. One would think that the introduction of an electron-withdrawing group to the aryl moiety would affect the α-bond more efficiently than the β-bond in such a way that a regioselective cleavage would be seen. This is actually not the case, and our data show that the nature of the substituent has only little effect on the length and the strength of both the α- and β-bonds. These small variations cannot account for the regioselectivity observed within this series of compounds, as discussed below.

If one uses the classical dissociative ET theory, the thermodynamics of a dissociative ET to a substrate RX would be described by the same eq 5. In the case of benzyl thiocyanates (**1a**−**f**), the thermodynamics would be in favor of an α-cleavage mainly because of the large difference in the bond dissociation energy between the α- and β-bonds and despite the very positive value of $E^0_{\mathrm{CN^\bullet/CN^-}}$ compared to $E^0_{\mathrm{NCS^\bullet/NCS^-}}$[20] (which favors a β-cleavage) as discussed above. These data show that, from a thermodynamic point of view, assuming no interaction between the produced fragments, the α-cleavage would be favorable for all compounds. If one considers the kinetics using eq 2 for such a concerted ET mechanism, the α-cleavage would again be favored mainly because of the large contribution of the BDE to the intrinsic barrier; the α-bond is about 50 kcal/mol weaker for all compounds. The solvent reorganization would also be in favor of the α-cleavage as discussed earlier. It seems then that using the classical dissociative ET theory, which is successfully applicable to concerted processes not involving the intermediate formation of radical/ion pairs (through radical/induced dipole interaction), an α-cleavage would be favorable from both a thermodynamic and a kinetic point of view for all compounds **1a**−**f**. Our data show that for this series of substituted benzyl thiocyanates, following a concerted ET mechanism (**1a**−**f**), only **1f** undergoes an exclusive α-cleavage upon electrochemical reduction. This indicates the involvement of other factors that have not been taken into consideration, for compounds **1a**−**e**, which could include the presence of a strong in-cage interaction between the β-cleavage produced fragments, as has been observed in the electrochemical reduction of chloroform and haloacetonitriles.[11] An investigation of the possible formation of radical/anion pairs and its effect on the observed regioselective bond cleavage during the electrochemical reduction process of benzyl thiocyanates (**1a**−**e**) has been launched.

Table 4. Interaction Energies and Minimum Energy Bond Lengths

$\mathrm{ArCH_2SCN}$	a_α[a] (Å)	a_β[b] (Å)	$D_{\mathrm{p}(\alpha)}$[c]	$D_{\mathrm{p}(\beta)}$[d]	ΔD_p
1a	3.0	2.6	0.073	0.447	0.374
1b	2.9	2.6	0.106	0.459	0.353
1c	2.9	2.6	0.137	0.471	0.334
1d	2.8	2.6	0.202	0.618	0.416
1e	2.9	2.6	0.154	0.495	0.341
1f	2.6	2.5	0.351	0.589	0.238
1g	2.1				
1h	2.0				

[a] Distance at minimum potential energy along the α-bond. [b] Distance at minimum potential energy along the β-bond. [c] Interaction energy ($E_{\mathrm{final}} - E_{\mathrm{minimum}}$) for the bond α (in eV). [d] Interaction energy ($E_{\mathrm{final}} - E_{\mathrm{minimum}}$) for the bond β (in eV).

Figure 3 shows the gas-phase potential energy[22] profile of the reduced forms of the studied compounds (**1a**−**h** + one electron) along both the α-and β-bonds. These energy profiles were calculated at the DFT/B3LYP/6-31G(P,D) level for different values of the α- (left figure) and β- (right figure) bond lengths starting from the already optimized structure of the studied thiocyanate (**1a**−**h**) + one electron.[23]

For compounds **1a**−**f**, all obtained curves have the shape of Morse curves and show a clear energy minimum along both the α- and β-bonds with different interaction energies (differences between the energy at long bond distances and the minimum energy). Values of the bond lengths at the minimum energy (a_α and a_β) as well as the interaction energies are reported in Table 4. These data show real trends, as it is clear that for compounds **1a**−**e** the interaction energies between the β-cleavage produced fragments are significantly higher than those between the α-cleavage produced fragments. Minimum energies are also observed at lower bond length values for the β-cleavage compared to the α-cleavage. An interesting result is the fact

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(21) Maartmann-Moe, K.; Sanderud, K. A.; Songstad, J. *Acta Chem. Scand. A* **1984**, *38*, 187.

(22) That represented on Figure 3a−h is not the absolute potential energy but rather the difference between the absolute value and a value lower than the minimum energy.

(23) Trials to perform a similar study by optimizing at each bond length value the reduced forms of the studied structures (**1a**−**h** + one electron) were unsuccessful as other bonds within the molecule were affected and sometimes even cleaved.

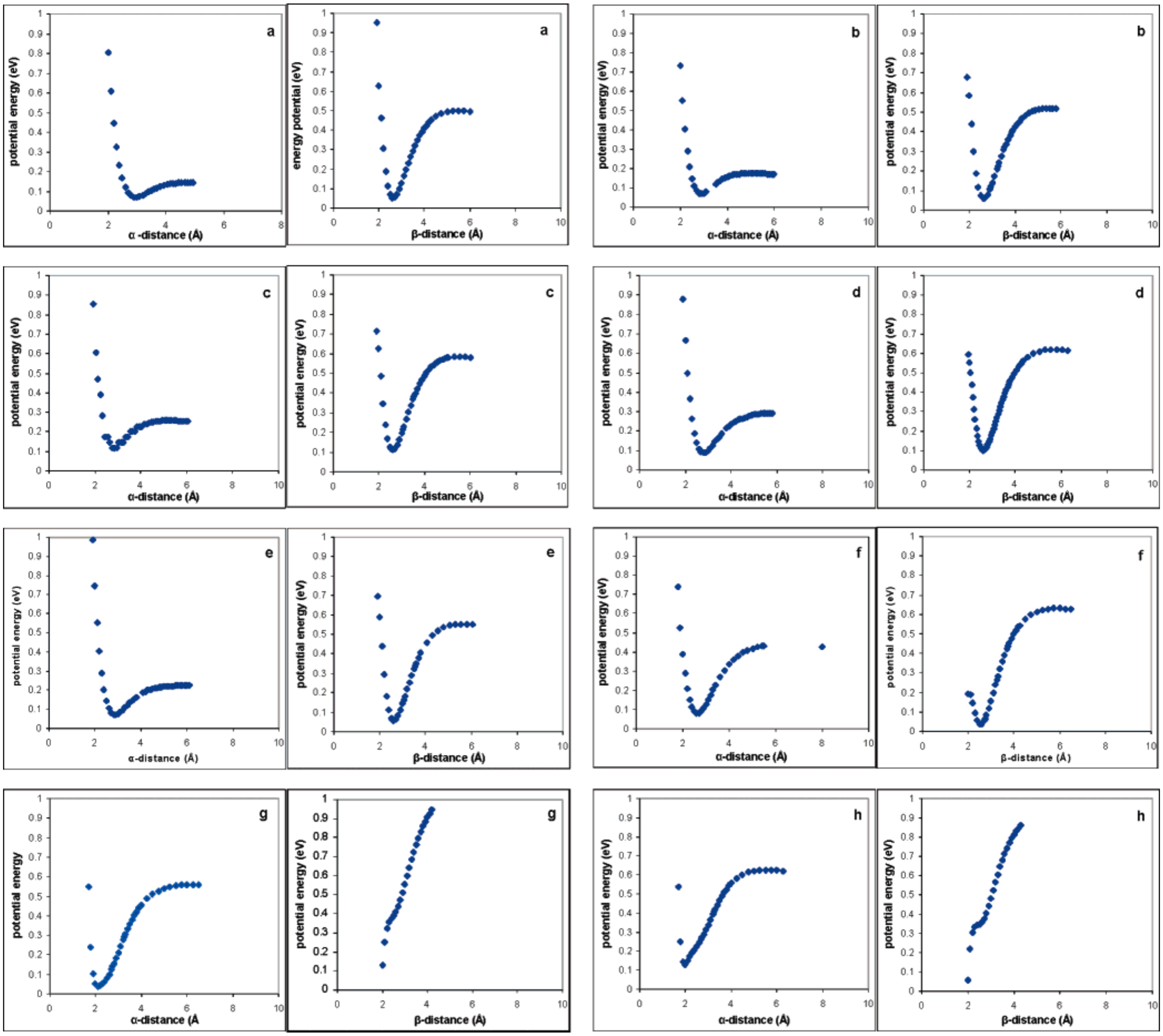

Figure 3. Calculated (B3LYP/6-31G(p,d)) potential energy profiles in the gas phase for the $XBn^{\bullet}/SCN^{-}$ pair (left) and the $XBnS^{\bullet}/CN^{-}$ pair (right) for (a) **1a**; (b) **1b**; (c) **1c**; (d) **1d**; (e) **1e**; (f) **1f**; (g) **1g**; and (h) **1h**.

that for the *p*-cyanobenzyl thiocyanate (**1f**), which according to our electrochemical data follows an ET mechanism similar to that for compounds **1a**−**e** but undergoes the exclusive reductive cleavage of the α-bond, a smaller difference (ΔD_p) between the interaction energies of the α- and β-cleavage fragments ($D_{p(\alpha)}$ and $D_{p(\beta)}$) is observed compared to the other compounds. For compound **1f**, with a stronger electron-withdrawing group, both $D_{p(\alpha)}$ and $D_{p(\beta)}$ increase, in agreement with what is expected;[11] however, the relative increase of $D_{p(\alpha)}$ is more substantial. For all compounds **1a**−**f**, and in both energy profile curves (along the α- and β-bonds), the minimum energies are observed at large distances (2.5−3 Å), suggesting the formation of radical/anion pairs rather than that of real radical anion intermediates. The minimum energy bond distances a_α are substantially larger than a_β, in agreement with the observed differences in the interaction energies D_p. It is worth noting that both a_α and a_β are smaller for **1f** than for the other compounds (**1a**−**e**) and that the relative decrease of a_α (for **1f** compared to **1a**−**e)** is larger than that of a_β. This is a clear indication that, at least in the gas phase, the interaction between the α-cleavage fragments for **1f** ($NCBn^{\bullet}$, SCN^{-}) is stronger than that for compounds **1a**−**e**.

A similar investigation for compounds **1g**,**h** (Figure 3g,h) shows that only the energy profile curves for the $XBn^{\bullet}/SCN^{-}$ pair (α-cleavage) show a minimum energy. Furthermore, these minima are observed at shorter distances of the α-bond (a_α) than those seen for compounds **1a**−**f** (Table 4), which indicates the formation of a real radical anion (**1g**,**h**$^{\bullet-}$) in the case of these two compounds. These data are in agreement with the electrochemical data which suggested the occurrence of a stepwise ET mechanism, involving the intermediate formation of a radical anion as a result of the injection of an electron into the parent molecules (**1g**,**h**), and showed the exclusive formation of products resulting from the α-cleavage.

In recapitulation, these calculations show that for compounds **1a**−**f** the interaction between the β-cleavage produced fragments is more important than that observed for the α-cleavage produced fragments. This interaction would counterbalance the advantage of the α-cleavage due mainly to the weak bond dissociation energy of the α-bond over the β one. As a result, the two processes (α- and β-cleavages) would be closer from a thermodynamic point of view than initially thought without the consideration of in-cage interactions. These calculations also show that in the case of **1f** the interactions are similar in both cases and that the main factor is still the bond dissociation energy, which is in favor of the α-cleavage. For compounds **1g**,**h**, the calculations are in complete agreement with the electrochemical data and the previous results considering a stepwise ET mechanism. A quantitative analysis would not be adequate because the calculations are done in the gas phase and do not take into consideration the solvent's effect and also because of the assumption made.[23] Qualitatively, however, these calculations show real trends that imply that the existence of a strong in-cage interaction through a sticky dissociative ET mechanism intermediate seems to be a possible explanation of the observed regioselective bond cleavage encountered in the reduction of compounds **1a**−**e**.

Conclusion

Important aspects of the electrochemical reduction of the studied substituted benzyl thiocyanates were investigated. A striking change in the reductive cleavage mechanism as a function of the substituent on the aryl ring of the benzyl thiocyanate is observed. With a nitro substituent (compounds **1g**,**h**), a stepwise mechanism involving the intermediacy of the radical anion takes place. With weaker electron-withdrawing or electron-donating substituents (CN, F, Cl, H, CH_3, CH_3O), a concerted mechanism is observed (compounds **1a**−**f**) on the basis of the analysis of the transfer coefficient (α) and the theoretical calculations. A similar behavior has been reported for benzyl halides.[19]

Unlike with aryl thiocyanates, the reduction of substituted benzyl thiocyanates **1a**−**e** involves no autocatalytic process, as shown by trace crossing in the electrochemical reduction of the aryl thiocyanates,[9a] even though both series yield the corresponding disulfides. The reason is that the disulfides **2a**−**e** are more difficult to reduce than the parent benzyl thiocyanates **1a**−**e**, and therefore, a second reduction peak is seen at a more negative potential.

More importantly, a regioselective bond cleavage is observed. A reductive α-cleavage (CH_2−S bond) is seen for compounds **1f**−**h** leading to the formation of the corresponding cyano- and nitro-substituted dibenzyls (**3f**−**h**). For compounds **1a**−**e**, both the α- and the β-bond (S−CN) could be cleaved as a result of an electrochemical reduction leading to the formation of the corresponding substituted dibenzyl disulfides (**2a**−**e**), substituted dibenzyl sulfides (**4a**−**e**), and substituted toluenes. These final products are generated through either a protonation or a nucleophilic reaction of the two-electron reduction-produced anion on the parent molecule.

No isomerization to the corresponding isocyanate has been observed during the electrochemical reduction of all substituted benzyl thiocyanates (**1a**−**h**).

The α-dissociation of the generated radical anions (**1g**,**h**$^{\bullet -}$) through a one-electron reduction of the corresponding nitro-substituted benzyl thiocyanates is favored over the β one from both a thermodynamic and a kinetic point of view.

Theoretical calculations in the gas phase show the existence of stronger interactions between the produced fragments for a β-cleavage than for an α-cleavage for compounds **1a**−**e** and seem to account for the encountered regioselective bond cleavage.

Finally, this study also shows another example of a sticky dissociative ET mechanism during the electrochemical reduction of benzyl thiocyanates (**1a**−**f**). In this example, the existence of in-cage interactions affects the outcome of the chemical reaction through the dissociation of a chemical bond that seems otherwise very stable.

Experimental Section

Cyclic Voltammetry. Electrochemical measurements were conducted in three electrode glass cells and thermostated at 25 °C under dry nitrogen. The working electrode is a 2 mm diameter glassy carbon electrode (Ekochemie). The electrode was carefully polished and ultrasonically rinsed with ethanol before each run. The reference electrode was SCE. The counterelectrode was a platinum wire. The electrochemical instrument used was an Autolab PGSTAT30 especially configured to carry high scan rate CV experiments. A feedback correction was applied to minimize the Ohmic drop between the working and reference electrodes.

Electrolyses. The electrolyses were carried out in 20 cm^3 cells with a glassy carbon (Electrosynthesis) rectangular plate working electrode of 4 cm^2. The counter electrode was a platinum grid, separated from the cathodic compartment by means of a glass frit. The reference electrode was the same as that for CV. The cell was thermostated at 25 °C, and the solution was kept under a nitrogen stream during the whole electrolysis. The disappearance of the starting material and the formation of the products were followed by in situ cyclic voltammetry. The supporting electrolyte, tetramethylammonium tetrafluoroborate (TMAF), was extracted, and chromatographic analyses (HPLC and GCMS) were performed by comparison with authentic samples of the product.

Chemicals. Acetonitrile (Aldrich), methyl sulfoxide (Fisher), tetramethylammonium tetrafluoroborate (TMAF), tetrabutylammonium tetrafluoroborate (TBAF) (Fluka, *puriss*), and silica gel (230−400 mesh, silicycle chem. div.) were used as received. 4-Methoxybenzyl mercaptan (Aldrich, 90%), 4-fluorobenzyl mercaptan (Alldrich, 96%), 4-methylbenzyl mercaptan (97%), 4-chlorobenzyl mercaptan (Aldrich, 98%), dibenzyl disulfide (Aldrich, 98%), dibenzyl sulfide (Aldrich, 98%), and hexamethyldisilazane (HMDS) (Aldrich, 97%) were used as received in the synthesis of the dibenzyl disulfides.

Benzyl thiocyanate (**1c**), *p*-methylbenzyl thiocyanate (**1b**), *p*-methoxybenzyl thiocyanate (**1a**), *p*-chlorobenzyl thiocyanate (**1d**), *p*-fluorobenzyl thiocyanate (**1e**), *p*-cyanobenzyl thiocyanate (**1f**), *p*-nitrobenzyl thiocyanate (**1g**), and *o*-nitrobenzyl thiocyanate (**1h**) were prepared by reacting their corresponding benzyl halides with potassium thiocyanate adsorbed on silica gel (230−400 mesh).[24]

Substituted dibenzyl disulfides (**2a**, **2b**, **2d**, **2e**) were prepared by oxidative coupling of their corresponding thiols using DMSO and hexamethyldisilazane (HMDS).[25] Substituted dibenzyl sulfides (**4a**−**e**), dicyano dibenzyl (**3f**), and dinitro dibenzyl (**3g**,**h**) were isolated from the electrolyzed solutions. Tetramethylammonium benzylthiolate was prepared in situ by electrolysis of the corresponding disulfide (**2a**).

Theoretical Calculations. The calculations were performed using the Gaussian 2003 package.[26] LUMO orbitals were calculated after a full optimization without imposed symmetry of the conformations using the UHF, B3LYP method with the 6-31G+(d,p) basis set starting from preliminary optimizations performed with semiempirical methods. We

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(25) Karimi, B.; Zareyee, D. *Synlett* **2002**, No. 2, 346.
(26) Frisch, M. J. et al. *Gaussian 2003*; Gaussian, Inc.: Pittsburgh, PA, 2003.

checked that the obtained conformations were real minima by running frequency calculations for the UHF and B3LYP calculations. These calculations could not be performed at the MP2 level because of the too large molecule sizes.

Acknowledgment. We thank Dr. John D. Goddard for a series of instructive discussions concerning the theoretical calculations. A. Houmam gratefully acknowledges the Natural Sciences and Engineering Research Council (NSERC), The Canada Foundation for Innovation (CFI), the Ontario Innovation Trust (OIT), and the University of Guelph for funding.

Supporting Information Available: Typical electrochemical behavior of substituted benzyl thiocyanates **1a**−**h**, electrochemical oxidation of tetrabutylammonium thiocyanate, and computational calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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