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J. Am. Chem. Soc., **2003**, 125 (42), 12676-12677• DOI: 10.1021/ja036710x • Publication Date (Web): 30 September 2003

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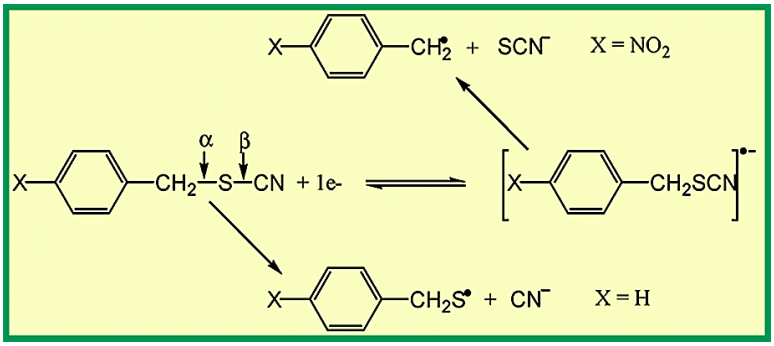

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J|A|C|S COMMUNICATIONS

Published on Web 09/30/2003

Regioselective Bond Cleavage in the Dissociative Electron Transfer to Benzyl Thiocyanates

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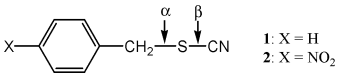
Since the introduction of the dissociative electron transfer (ET) theory[1] much attention has been given to understanding whether ET and bond breaking are concerted or successive steps and to factors controlling the occurrence of either mechanisms.[2] According to this theory, the reaction activation energy depends on both thermodynamic and kinetic factors, through a quadratic activation−driving force relationship.[1] The difference in the reaction free energy between the two ET mechanisms can be expressed by the corresponding standard potentials (eq 1).

$$E^0_{RX//RX^{\bullet-}} - E^0_{RX/R^{\bullet}+X^{\bullet-}} = E^0_{RX/RX^{\bullet-}} + D_{R-X} - E^0_{X^{\bullet}/X^-} - T\Delta S_{RX/R^{\bullet}+X^{\bullet}} \quad (1)$$

The weaker the bond and the more positive $E^0_{X^{\bullet}/X^-}$, the more favorable the thermodynamics of the concerted mechanism are. The intrinsic barrier contains solvent and inner reorganizations ($\Delta G_{0,s}^{\ddagger} + \Delta G_{0,i}^{\ddagger}$). For a concerted ET, the main contribution to $\Delta G_{0,i}^{\ddagger}$ is that of the bond dissociation.[1,2] In most reported studies, however, the same bond (R−X) is broken when the ET driving force is changed for a series of compounds.[2] While regioselective bond cleavage in dissociative ET reactions has been reported, concrete examples are however limited, and the factors controlling the regioselectivity remain unclear.[3] We recently 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.[4] Here we report the electrochemical reduction of benzyl (**1**) and *p*-nitrobenzyl (**2**) thiocyanates. Not only is a change of the ET mechanism observed, but more interestingly, a clear-cut example of a regioselective bond cleavage is also encountered. Furthermore, we show that both phenomena may be understood on the basis of the dissociative ET theory and its extension to the formation/dissociation reactions of radical ions.[1b,2]



The cyclic voltammetry of benzyl thiocyanate (**1**) in acetonitrile (Figure 1a) displays an irreversible reduction peak at a potential $E_p = -2.20$ V vs SCE. The peak width[4] has a value of 160 mV. The variation of the peak potential with the log(ν) is linear with a slope equal to 94 mV per unit log(ν). This first reduction peak corresponds to the consumption of one electron per molecule. A second irreversible reduction peak is observed at −2.53 V vs SCE and corresponds to the reduction of dibenzyl disulfide (Figure 1a). The coefficient transfer values determined from both the first reduction peak width[4] and from the E_p − log(ν) plot[4] correspond to 0.29 and 0.31 respectively, i.e., much lower that 0.5, indicating a reaction kinetically controlled by an irreversible electron-transfer step.[1,2] The initial ET and the S−CN bond breaking (β-cleavage) are concerted; the produced radical thiyl is immediately reduced at the electrode, yielding the benzyl thiolate anion. As for the aryl thiocyanates, the benzyl thiolate reacts on **1** to yield dibenzyl disulfide (Scheme 1). An important result here is the absence of autocatalysis, shown by trace crossing in the electrochemical reduction of the aryl thiocyanates. The reason being that dibenzyl disulfide is more difficult to reduce than **1**.

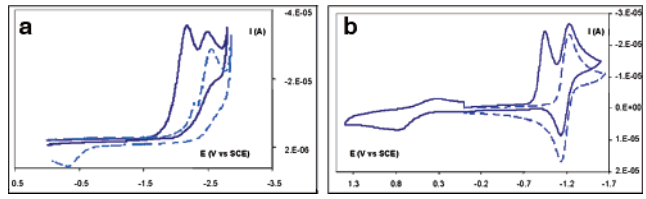
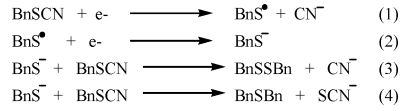


Figure 1. Cyclic voltammetry in CH_3CN/TBAF (0.1 M) at a glassy carbon electrode, $\nu = 0.2$ V/s, temperature = 20 °C of (a) **1**: 2.35 mM (——), **3**: 1.3 mM (- - -) and (b) **2**: 2 mM (——), **5**: 1.5 mM (- - -).

Scheme 1



Electrolysis of **1** confirmed the stoichiometry of 1 electron per molecule and the formation of dibenzyl disulfide (**3**: 72%); it shows further the formation of dibenzyl sulfide (**4**: 26%) which results from the attack of the benzyl thiolate on the benzylic carbon of **1** with the ejection of thiocyanate anion. This has been confirmed by a control reaction where tetrabutylammonium benzyl thiolate and **1** have been mixed to yield both **3** and **4**.[5]

The cyclic voltammogram of *p*-nitrobenzyl thiocyanate (**2**) displays an irreversible reduction peak at a potential $E_p = -0.96$ V vs SCE (Figure 1b). Its height corresponds to the consumption of 1 electron per molecule. The peak width has a value of 72 mV and the slope of the E_p vs log(ν) plot is equal to 48 mV per unit log(ν). These peak characteristics correspond to a stepwise ET involving the intermediacy of a radical anion and with a mixed kinetic control by both the ET and the bond dissociation steps. This first irreversible peak is followed by a second reversible peak ($E^0 = -1.19$ V vs SCE) corresponding to the reduction of 4,4′-dinitrodibenzyl (**5**), by comparison with an authentic sample (Figure 1b), formed as a result of a chemical reaction following the ET where the thiocyanate anion is the leaving group (α-cleavage) and not the cyanide as seen for compound **1** in agreement with previous studies.[6] Electrolysis of **2** confirmed the stoichiometry of 1 electron

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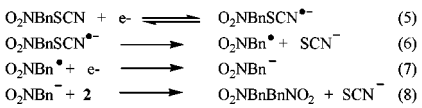
10.1021/ja036710x CCC: $25.00 © 2003 American Chemical Society

per molecule and showed the formation of 4,4′-dinitrodibenzyl quantitatively with no isocyanate.[7,8] Furthermore, in the presence of excess of phenol, the electrolysis of **2** yields exclusively 4-nitrotoluene, and the stoichiometry increases to 2, indicating that **5** is the result of a nucleophilic attack of *p*-nitrobenzyl anion on **2** (Scheme 2).

Scheme 2



A theoretical study at the B3LYP level clearly shows that while the LUMO for **1** is spread all over the molecule, the LUMO for **2** is more located on the aryl moiety with a lower coefficient on the SCN group (Figure 2), suggesting that in the latter case the incoming electron is hosted by the π^* of the aryl. In the framework of the dissociative ET theory, the ET mechanism difference between **1** and **2** can be understood on the basis of thermodynamic considerations. The introduction of a nitro group lowers the LUMO of the aryl moiety; once the radical anion (**2**$^{\bullet-}$) is formed, the electron will be transferred from the π^* to the σ S−CN bond in a heterolytic mode.[2] For **1**, the incoming electron would be directly injected into the σ S−CN bond simultaneously with its dissociation in a concerted ET mechanism. This is in agreement with what has been reported earlier for benzyl halides[2] and with the difference in the calculated LUMO for **1** and **2**. If one considers the reduction products, it is clear that besides the gain in the standard reduction potential of **2** due to the introduction of the nitro group, the biggest effect is due to the huge difference (1.6 V) between the oxidation potentials of the two leaving groups.[9]

Figure 2. LUMOs for **1** and **2**.

The decomposition of **2**$^{\bullet-}$ can be understood by considering the extension of the dissociative ET to the decomposition of radical anions.[1b,2] Here again the thermodynamics would be in favor of a β-cleavage mainly due the very positive value of $E^0_{CN\bullet/CN^-}$ compared to that of $E^0_{SCN\bullet/SCN^-}$,[9] which will be very hard to overcome by a more favorable bond dissociation energy in the case of an α-cleavage. This is because the nitro group will only slightly decrease the α BDE, and for compound **1** the leaving group's effect predominates. The intrinsic barrier for the decomposition of **2**$^{\bullet-}$ involves rather the dissociation energy of the β bond at the level of the radical anion **2**$^{\bullet-}$. The solvent reorganization energy would not be very different for the two dissociation modes (α and β).[1b,2] With the π^* orbital of the aryl moiety being the electron hospitable orbital in the reduction of **2**, the dissociation follows a heterolytic[2] cleavage, and the contribution of the bond dissociation to the intrinsic barrier of the decomposition of **2**$^{\bullet-}$ can be described by eq 2, showing a total independence on the leaving's group oxidation potential, which is the major factor between the α and β cleavages in terms of driving force. $E^0_{O_2NBn\bullet/(O_2NBn\bullet)^{\bullet-}}$ and $E^0_{O_2NBnS\bullet/(O_2NBnS\bullet)^{\bullet-}}$ would not be very different since they both represent the injection of one electron in the π^* orbital of *p*-nitrophenyl moiety. In this case, the bond dissociation energy, which is in favor of an α-cleavage, becomes a predominant factor.[10]

$$\Delta G^{\ddagger}_{0,RX\bullet^-/R\bullet+X^-} = \frac{1}{4}(D_{R-X} + E^0_{RX/RX\bullet^-} - E^0_{R\bullet/(R\bullet)^{\bullet-}} + T\Delta\bar{S}_{RX\bullet^-/R\bullet+X^-}) \quad (2)$$

It appears that **2**$^{\bullet-}$ undergoes an α-cleavage by a counter-thermodynamic process[11] but with a more advantageous intrinsic barrier, the S−CN bond being stronger. The particular role of the intrinsic barrier in the reduction of **2** is due to the difference in the ET mechanism; the stepwise mechanism being characterized by a smaller driving force, the activation free energy is more "sensitive" to changes in the intrinsic barrier. With a much higher driving force for **1**, the concerted β-cleavage occurs despite a more favorable intrinsic barrier for the α-cleavage.[12] Thus, the introduction of the nitro substituent to the phenyl ring decreases the driving force, mainly by lowering the energy of the LUMO and to a lesser extent by weakening the C−SCN bond, both factors favoring the α-cleavage. A more expanded series of benzyl thiocyanates is being synthesized. Quantitative analyses concerning their kinetics and thermodynamics will be reported.

Acknowledgment. A.H. gratefully acknowledges the NSERC (Canada), the Canada Foundation for Innovation (CFI), and the Ontario Innovation Trust (OIT).

Supporting Information Available: Electrochemical data and LUMO calculations for **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA036710X