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Review

# Electron Transfer Initiated Reactions: Bond Formation and Bond Dissociation

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# Electron Transfer Initiated Reactions: Bond Formation and Bond Dissociation

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## 1. Introduction

Electron transfer reactions are among the most elementary of all chemical reactions and play a fundamental role in many areas including organic synthesis, biological processes, novel energy sources, energy storage devices, amperometric sensors, etc. A field that has attracted considerable attention is that involving electron transfer to organic and bioorganic molecules. In such reactions, electron transfer is very often accompanied by the formation of new chemical bonds and/or the dissociation of existing ones. A wide variety of chemical transformations that are initiated by a single initial

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Abdelaziz Houmam was born and grew up in Casablanca in Morocco. After obtaining his BSc. degree from the Faculté des Sciences I, Université Hassan II, in Casablanca, he joined Prof. Jean-Michel Savéant's laboratory at the University of Denis Diderot (Paris 7) in Paris, France, where he obtained his Diplome d'Etudes Approfondies (DEA) and his Doctorate under the supervision of Prof. Jean Pinson. He then worked as a research associate at the Steacy Institute for Molecular Sciences (SIMS) at the National Research Centre (NRC) in Ottawa with Dr. Dan Wayner. In 1998, he joined McGill University in Montreal as a research associate in Prof. Bruce Lennox's research group. In 2000, he accepted an assistant professor position at the University of Guelph, where he is actually an associate professor. His general research interests lie in the area of organic and interfacial electrochemistry.

electron transfer are described in the literature and can be encountered under both oxidative and reductive conditions. Unraveling the nature of the fundamental steps involved in the electron transfer and the subsequent reactions has always been an essential step toward reaching a molecular understanding of these processes. In these multiple step reactions important questions arise concerning not only their mechanisms and the factors controlling them but also the associated energies and kinetics and any similarity to certain non-electron transfer processes. Extensive studies have already shed considerable new light on many of these important questions.

This review is intended to provide an up to date description of some of the important aspects and recent fundamental advances of these reactions including the chemistry, the techniques used, the principal mechanisms and their dichotomy with other polar mechanisms.

Indeed considerable progress has been achieved in understanding electron transfer initiated bond formation and/or bond breaking reactions. From a mechanistic standpoint, the electron transfer step in these reactions can be classified into two main pathways. In the first mechanism, the bond formation or dissociation occurs subsequent to the initial electron transfer process, and involves either an oxidized or a reduced species of the parent substrate that only undergoes a degree of reorganization and no bond disruption. The Marcus theory of outer-sphere electron transfer, which provides a description of the electron transfer process in its basic format, when it is not coupled with chemical changes involving the disruption of chemical bonds, still applies. This theory provides a description of the electron transfer process through a kinetic−thermodynamic relationship. Progress made in the fundamental understanding of electron transfer processes has made it possible not only to distinguish between processes associated with different degrees of reorganization (and interconversion) but also to account for the structural changes involved. It has also allowed distinction to be made between processes involving different degrees of donor−acceptor interactions in the transition states.

For both these mechanisms we shall adopt Savéant's terminology which is an extension of the initial definition regarding inorganic centers made by Taube. Regardless of whether a bond is formed and/or cleaved in a subsequent chemical step or not, these will be referred to throughout this review as "outer-sphere electron processes". Considering the IUPAC definition, "inner-sphere electron transfer reactions" were historically defined as those taking place between metal centers sharing a ligand or atom in their respective coordination shells. The definition has been extended to any situation in which the interaction energy between the donor and acceptor in the transition state is significant (>20 kJ/mol). Reactions where the electron transfer step is a concerted process concomitant with the formation and/or dissociation of a chemical bond, which is in the second mechanism, fall in this category. The Marcus theory can no longer account for such processes since structural disruption rather than reorganization is involved. The simultaneous dissociation of a chemical bond upon addition or removal of an electron is now a well-understood process thanks to the "dissociative electron transfer theory" formulated by Savéant.

The ability to unravel the more intricate details of electron transfer (ET) reactions has greatly benefited from the widespread interest that the chemistry of reactive intermediates including radicals, ions and radical ions has attracted in recent decades. The considerable amount of experimental and theoretical data concerning these reactive intermediates that has become available has allowed a more accurate analysis of the dynamics of such ET reactions. Evidence for the potential formation of ion pairs or $\sigma$-radical ions in electron transfer reactions has not only been confirmed but has also been rationalized through extension of the existing theories. Accordingly, the effect of the interaction between fragments and the formation of $\sigma$-radical ion intermediates on the dynamics of ET processes can now be predicted and quantified. As a result, ET reactions where such phenomena are present have not only been shown to be faster and easier, but have also been shown to change if they involve competitive processes. In addition, the chemistry of these intermediates has also benefited from these developments. The dynamics of the formation and decomposition of radicals, ions and radical ions have all been described in terms of ET theories: principally through extension of the dissociative electron transfer (DET) theory.

Not surprisingly the important progress made in understanding ET reactions has meant that certain processes traditionally believed to be polar in nature were questioned and hence ET reactions have been expanded to cover new systems. While many such examples are available for discussion, we shall limit ourselves in this review to the degree of involvement of single electron transfer (SET) in $S_N2$ nucleophilic substitution reactions. Factors controlling the dichotomy between the two processes as well as the nature of these reactions pathways have been extensively investigated both theoretically and experimentally. Another focus of this review will cover the issue of long-range dissociative ET. Even if long-range ET in organic and bioorganic molecules has attracted considerable interest for a long time; it was not until recently, however, that these processes were investigated with respect to bond cleavage and bond formation reactions. While this field is still somewhat in its infancy, the accumulative knowledge regarding long-range ET processes and DET is of great importance.

## 1.1. Scope of the Review

Although ideally a review such as this aims to deal with all the aforementioned issues regarding ET reactions involving the formation and/or dissociation of chemical bonds, there are restraints, and since many monographs and reviews covering some of these topics, to different degrees, are available, we have set limits. I would therefore like to take this opportunity to acknowledge all my fellow researchers whose work is beyond the scope of this manuscript. A complementary review concerning proton-coupled ET reactions is available in this issue.[1] Only a few illustrative examples of ET-initiated bond dissociation and bond formation reactions will be presented in section 2. These will be classified into reductive and oxidative processes. Examples involving the interconversion of electron transfer generated species will also be presented briefly.

Important advances in this field have been principally the result of progress covering two major aspects. The first is related to the continuous improvement of existing techniques to study ET-initiated reactions as well as the development of new ones. The second concerns the tremendous progress made in the fundamental understanding of ET reactions through the development of ET theories and their continuous expansion.

Hence, it is pertinent that a brief survey of the major methodologies used to study bond breaking and bond formation reactions resulting from ET initiation will be provided in section 3. These techniques will be discussed in relation to their initiation modes and will include thermal, electrochemical, photochemical and solvated electron methodologies. Determination of the parameters relevant to the dynamics and mechanisms of the reactions involved will also be briefly discussed.

In section 4, the fundamental aspects of outer-sphere and inner-sphere electron transfer processes, through both thermal and electrochemical initiations, will be discussed in light of current theories including Marcus theory and Savéant's DET theory. Indeed two situations need to be considered when considering ET bond cleavage and bond formation reactions. The bond breaking or formation may take place either simultaneously with or in a successive step to the ET step. In the latter case, ET is accompanied by a structural internal reorganization only and does not involve any bond cleavage or formation. Particular examples where other parameters may have an impact on the dynamics of the ET reaction mechanism such as cluster formation or $\sigma$-radical ion involvement will also be discussed in this section. Because an increasing number of systems involving cluster formation ("sticky" DET mechanism) are being found, some recent examples will be discussed in more detail.

The question of whether the two steps are concerted or successive and the ability to assign a particular mechanism are important issues that will be addressed in section 5. A comparison with photoinduced ET reactions will also be discussed in the same section for two important reasons. One is that the initiation mode may affect the ET mechanism, and the other is related to the fact that the tools used to discriminate between the two mechanisms differ from one initiation mode to the other. Intramolecular DET will be the subject of section 6. This will include a review of the extension of the DET theory to the formation and dissociation of radical ions as well as a discussion of the dissociation mechanisms and the factors controlling them. Long-range ET coupled with chemical transformations, which has recently attracted increasing attention, will also be reviewed in this section, and relevant experimental examples will be presented.

**Scheme 1. Reductive Cleavage of Aryl and Alkyl Halides**

$$\mathrm{ArX} + \mathrm{e}^- \rightleftharpoons \mathrm{ArX}^{\bullet-} \qquad \mathrm{RX} + \mathrm{e}^- \longrightarrow \mathrm{R}^{\bullet} + \mathrm{X}^-$$

$$\mathrm{ArX}^{\bullet-} \longrightarrow \mathrm{Ar}^{\bullet} + \mathrm{X}^- \qquad \mathrm{R} = \text{alkyl},\ \mathrm{Ar} = \text{aryl},\ \mathrm{X} = \text{halogen}$$

Studies have shown that SET processes may in fact be key steps in other chemical reactions originally believed to involve the movement of pairs of electrons, in other words, polar reactions. In this context nucleophilic substitutions provide the best example. Hence section 7 will be dedicated to a discussion of the dichotomy between the $S_N2$ mechanism and single electron transfer in nucleophilic substitution reactions of alkyl halides. Experimental as well as theoretical aspects of this dichotomy will be discussed.

# 2. Bond Cleavage and Bond Formation in Electron Transfer-Initiated Reactions

It is well established that electron transfer processes form the origin of many important reactions: nucleophilic substitutions, Grignard additions, metal hydride reductions, and cycloadditions are some of many such reactions.[2–5] The reason behind this is the fact that the addition or removal of an electron readily leads to the cleavage of an existing chemical bond or the formation of a new one. In certain cases this can be preceded by reorganization of the ET intermediate. The nature of the process that eventuates depends on the structure of the reactant itself, on the nature of the initiation (oxidation vs reduction) and on the reaction conditions which include the solvent, pH, and any other reagents. In addition to representative examples presented in this section readers are referred to the extensive available literature.[2–5]

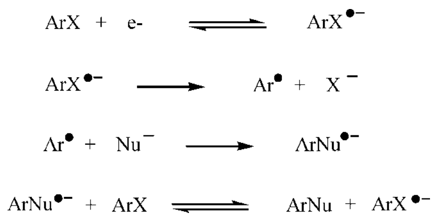
## 2.1. Electron Transfer-Initiated Bond Cleavage

One of the most investigated processes in chemistry is ET-initiated bond cleavage, which will be referred to throughout this manuscript as "dissociative electron transfer" (DET). Bond dissociation can result from either reduction or oxidation of the initial reactant, and the two processes (electron transfer and bond dissociation) can take place either simultaneously or as two successive steps.

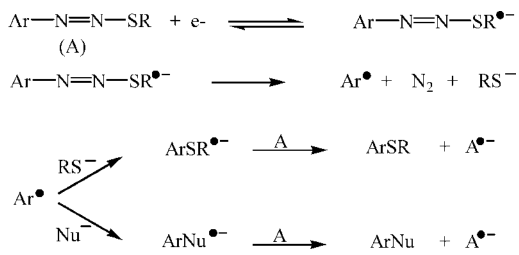
### 2.1.1. Reductive Processes

Bond cleavage following reduction of the initial reactant has been shown to take place for a wide variety of species including neutral structures, ions and radicals. Reductive DET has been shown to lead to the dissociation of a large variety of chemical bonds including C−C,[6–22] C−S,[23–31] C−O,[32–42] C−N,[43–46] O−O,[47–51] N−S,[43–46] N−O,[52–59] S−S,[60–66] S−O,[67] C−halogen,[68–77] N−halogen,[78–80] and S−halogen,[81–83] among others. The most investigated reductive ET-initiated cleavage process is probably the reduction of organic halides (Scheme 1). It is interesting to note that while the reduction of alkyl halides[68–73] has been shown to undergo a reductive cleavage where the two processes are simultaneous, aryl halides,[74–77] on the other hand, involve,

**Scheme 2. $S_{RN}1$ Reaction Mechanism**



**Scheme 3. Reduction Mechanism of Aryl Azo Sulfides in the Presence of an External Nucleophile**



in general, the intermediacy of a radical anion intermediate and two successive steps.

The intermediate formation of a radical anion that subsequently dissociates in solution, regardless of the initiation mode, has been exploited in many cases to develop efficient methods for the synthesis of valuable chemicals. An interesting example in this context is the $S_{RN}1$ reaction (Scheme 2), where the radical generated through a reductive cleavage is trapped by a nucleophile present in the solution.[77] The overall reaction is a chain nucleophilic substitution process that is catalytic in electrons even if it requires an ET initiation.

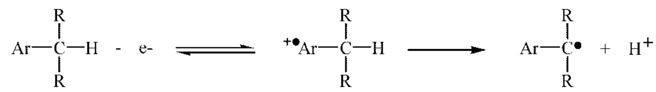
The ET-initiated cleavage of aryl azo sulfides[43–46] is another example worth mentioning. Injection of an electron results in the dissociation of both the C−N and N−S bonds through ejection of a molecule of nitrogen. This is followed by recombination of the resulting aryl radical and thiolate to generate a sulfide. Addition of an external nucleophile has been shown to compete with the thiolate anion recombination, and hence other products were obtained. High concentrations of the external nucleophile may be required (Scheme 3). This approach has been efficiently used toward the determination of kinetic data of the nucleophilic attack reaction.

It should be noted that the reduction of diazonium salts[85,86] also leads to the ejection of a molecule of nitrogen and the generation of a radical. The electrochemical reduction of diazonium salts is actually one of the most efficient methodologies for the grafting of organic molecules onto conducting and semiconducting surfaces. The facile electrochemical reductive cleavage of the diazonium cation produces a radical that is more difficult to reduce thus allowing its reaction with the carbon surface at the potential where it is produced.[85–101]

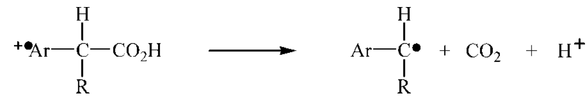
### 2.1.2. Oxidative Processes

Removal of an electron from the reactant can lead to the weakening of a chemical bond hence promoting its cleavage. Examples include the dissociation of C−H, O−H, and C−C,[102–108] C−S,[109–115] N−O and C−Si[116] chemical bonds. This process has been investigated not only on a fundamental level through analysis of the dynamics and mechanisms of these reactions as well as factors controlling them but also on a practical level through study of their importance in areas including synthesis,[117–121] polymerization[122] and photosensitization.[123,124]

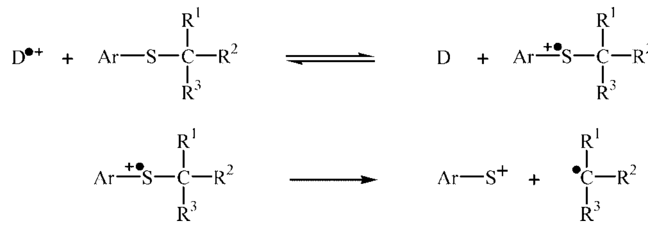
**Scheme 4. Oxidative Deprotonation of Substituted Aromatic Compounds**



**Scheme 5. Oxidative Decarboxylation of Aromatic Carboxylic Acids**



**Scheme 6. Oxidative Dissociation of Alkyl Aryl Sulfides**



Elimination of a proton following oxidation of a reactant is a well-documented reaction, and extensive examples are available in the literature.[103,108,125] Electrochemically initiated reactions have been widely investigated since they can be used as a source of electrogenerated acids.[126] Elimination of a proton has also been used in the anodic substitution of C−H bonds.[4] Alkyl aromatic compounds[127–136] (Scheme 4) have been the most widely investigated reactants since the oxidative bond dissociation is an efficient route to their side chain oxidation leading principally to the corresponding aromatic aldehydes.

Cleavage of the O−H bond in alcohols under oxidative conditions has also been studied both experimentally[136−138] and theoretically,[139] and the reaction has been shown to be strongly dependant on the pH of the electrolytic solution.

Another well-documented example is the C−C dissociation in ET-generated radical cations.[102,140–142] An interesting example of a C−C bond cleavage under oxidative conditions is the decarboxylation of radical cations (Scheme 5).[125–127,143] Kinetic studies illustrating the effect of neighboring groups,[144] the redox properties of the parent reactant[145] and the nature of the medium[146,147] have all been reported.

The dissociation of the C−S bond in aryl alkyl sulfides (Scheme 6) has also attracted considerable attention. Laser flash photolysis proved particularly interesting as it allowed measurement of the rate constants of the ET-generated radical cations. The influence of the C−S bond dissociation energy, as a function of the alkyl substituent, on the kinetics of the cleavage reaction has been studied in depth.[115,148]

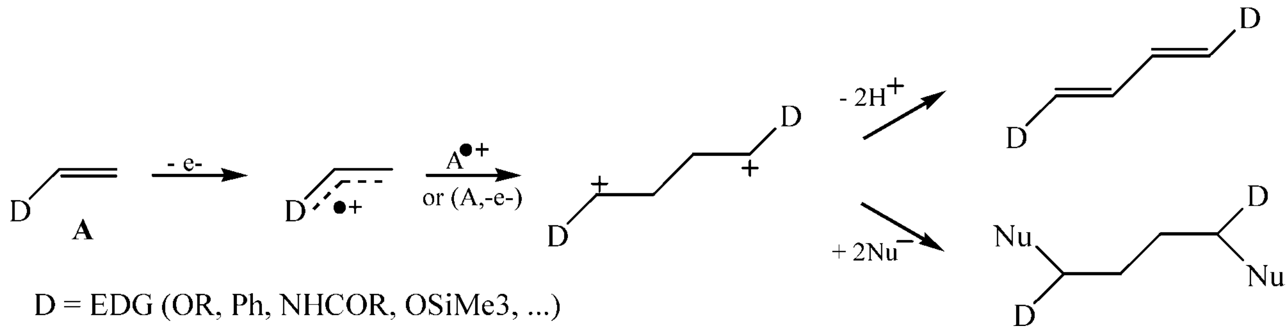
## 2.2. Electron Transfer-Initiated Bond Formation

The formation of a new chemical bond can also be readily initiated by an ET step. Like dissociation, this process can result from either a reduction or an oxidation. One difference, however, is that, unlike dissociation, bond formation takes place in a separate step after the ET initiation.

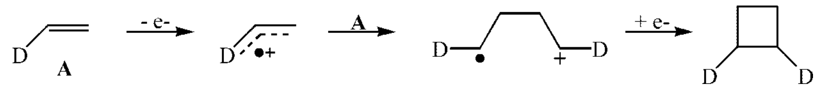
### 2.2.1. Oxidative Bond Formation

This process has also been widely investigated. The addition of an electron-rich molecule to an oxidized species

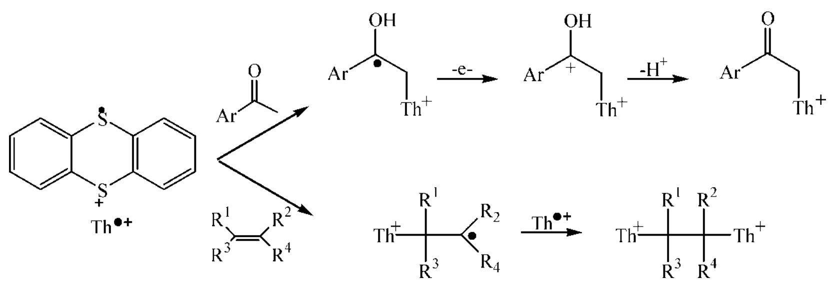
**Scheme 7. Oxidative Dimerization of Alkenes**




**Scheme 8. Oxidative Cycloaddition of Alkenes**




**Scheme 9. Oxidative Formation of C−S Bond in the Synthesis of Thianthrenium Salts**



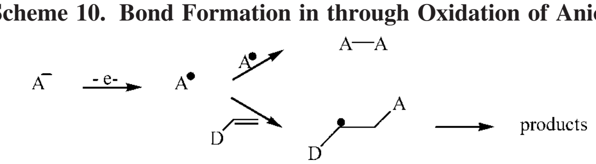

such as a radical cation is one of the most commonly reported. The oxidative coupling of electron-donating substituted alkenes is a well-known process.[4,149–152] The coupling takes place at the level of the radical cation generated by the oxidation of the parent molecule with either another radical cation or even the parent olefin. In the latter case another ET usually takes place, especially under electrochemical conditions. Depending on the medium, the dication generated may undergo either deprotonation or further bond formation through reaction with nucelophilic species in solution (Scheme 7).

Olefins also undergo cycloaddition reactions through a similar mechanism involving the formation of a new chemical bond in a step subsequent to the ET oxidation (Scheme 8).

Scheme 9 illustrates an interesting example of the oxidation of thianthrene in the presence of a methyl ketone or an alkene. In both cases a new S−C chemical bond is formed through reaction of the electron-rich molecule with the thianthrene radical cation. While the reaction leads to the formation of keto-thianthrenium salts in the presence of methyl ketones, in the presence of alkenes dithianthrenium salts form as a result of the addition of a thianthreniun radical cation to each side of the double bond. The thianthrene radical cation is readily formed through oxidation either homogeneously in solution[153–168] or electrochemically.[169] Thianthrenium salts have been obtained using both methods,[162,163,165] although bisulfonium salts were only isolated through electrolysis. The use of cyclic voltammetry and electrolysis techniques made it possible to determine the detailed mechanisms and estimate the rate constant for the addition reaction (formation of the C−S bond).[169]

Radicals generated through the one-electron oxidation of the corresponding anions have also been widely investigated in electron-initiated bond formation reactions.[170] Dimerization and

**Scheme 10. Bond Formation in through Oxidation of Anions**




addition to electron-rich reagents such as olefins are the main processes (Scheme 10). Such reactions can lead to the formation of a large variety of chemical bonds. Polymerization through radical cation coupling is also another possible pathway that has been identified and exploited in particular for the synthesis of conducting polymers.[171,172]

### *2.2.2. Reductive Bond Formation*

Bond formation in reductive processes is a common reaction. Reduced species such as anions and radical anions can undergo a variety of chemical additions, in particular, protonation, dimerization, and nucleophilic addition.

The well-known Birch reduction is a good example of the protonation of radical anions generated through reductive electron transfer to aromatic compounds.[173] The mechanistic details of the protonation reaction of electrochemically-generated radical anions and their subsequent steps, mainly through ECE or DISP mechanisms, have been intensively investigated (Scheme 11).[174–180] The ECE and DISP mechanisms are closely related since they both involve an initial heterogenous ET (between an electrode and an initial species) followed by a homogeneous first-order, or pseudo-first-order, reaction. The difference between the two mechanisms resides in the nature of following step as shown in Scheme 11. Although in both cases the subsequent step is an ET involving the product of the homogeneous chemical step ($AH^{\bullet}$ in this case), in the ECE mechanism this ET is heterogenous and takes place at the surface of the electrode, while in the DISP mechanism, it is a disproportionation

**Scheme 11. Protonation of Electron Transfer Generated Radical Anions**

$$A + e^- \longrightarrow A^{\bullet -}$$

$$A^{\bullet -} + H^+ \longrightarrow AH^{\bullet}$$

$$AH^{\bullet} + e^- \longrightarrow AH^- \quad \text{(ECE)}$$

$$AH^{\bullet} + A^{\bullet -} \longrightarrow AH^- + A \quad \text{(DISP)}$$

reaction that takes place in solution and involves also the product of the initial ET ($A^{\bullet -}$). These and other important electron transfer overall mechanisms have been extensively studied.[181–185]

The formation of a chemical bond through the electrodimerization of a species, generated through the reduction of a parent molecule, is a well-established process. The electrodimerization of acrylonitrile, shown to involve the coupling of two radical anions, is probably the best known example.[186–189] Another well-investigated example is that regarding the dimerization of ketyls through reduction of the corresponding carbonyl compounds.[190] Reversible reductive dimerization has also been investigated.[191–195]

The alkylation reaction of radical anions, generated through reduction using alkyl halides, is another interesting example.[196–198] This reaction is an undesirable process in the homogeneous redox catalysis of alkyl halides because it consumes the redox mediator and hence inhibits the catalytic reaction (see section 3). Ammonium and sulfonium salts have been shown to undergo similar reactions with radical anions.[199] Both nucleophilic attack, through either an $S_N1$ or $S_N2$ process, and a single ET between the radical anion and the alkyl halide have been shown to be potential routes to the alkylated product. This will be discussed in more detail in section 7.

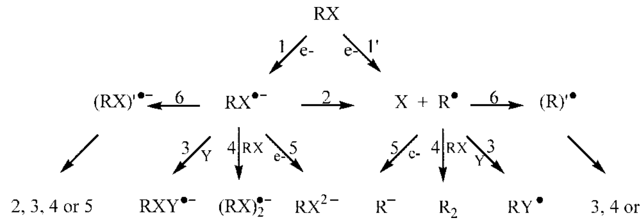
Radical anions generated via reductive ET have also been reported as reacting with many other reagents through an initial bond formation. With carboxylic acid derivatives such as esters, anhydrides, amides and nitriles, the reaction has been shown to lead to the acylated products.[200,201] Carboxylation and sulfonation of unsaturated compounds through the reaction of the radical anions formed with $CO_2$ and $SO_3$ provides another classical example of bond formation as the second step following an initial reductive ET.[202–206]

## 2.3. Rearrangement of Electron Transfer Products and Intermediates

The immediate product of an electron transfer step can in specific cases undergo significant conformational changes. Many examples are available in the literature, and these include isomerization of the radical anions of *cis*-stilbene,[207] *cis*-azobenzene[208,209] and tetraalkylhydrazines.[210–214] In the case of *cis*-stilbene isomerization has been shown to involve the dianion.[215] Another interesting example where a dianion, produced through reduction, undergoes significant interconversion leading to a more stable intermediate is that of 1,6-dimethylbicyclo[4.4.1]undeca-2,4,7,9-tetraene.[216,217]

Tetraphenylethylenes have also been shown to involve the formation of an intermediate radical anion that undergoes substantial interconversion.[218–221] For octatetraenes which have shown similar behavior[222–224] the electron transfer is usually slower than for compounds undergoing less conformational changes.

**Scheme 12. Major Electron Transfer Reaction Pathways**




## 3. Initiation Modes and Experimental Methodologies

A very important aspect of ET reactions is that they can be initiated by a variety of procedures. These include thermal (homogeneous and heterogeneous), photochemical and through use of solvated electrons as in pulse radiolysis. This has stimulated the development of a wide range of techniques and analytical methodologies for the study of ET reactions with a view to gaining insights into various aspects of their dynamics and mechanisms. All these techniques have an obvious common factor: the addition or removal of an electron to or from a reactant. But the fact that their similarity may end here means that sometimes these techniques provide different information regarding such ET-initiated reactions. They differ in terms of the analysis time windows thus making them useful for different systems and capable of studying different types of intermediates. The other issue concerns the fact that the initiation step itself, as well as subsequent steps, may differ from one initiation technique to another despite the fact that in all cases an electron is added or removed. As a result the chemistry following the initial ET step may differ totally from one initiation mode to another. So while thermal homogenous initiation is a reaction usually leading to the transfer of a single electron, electrochemical initiation is a heterogeneous process very often involving the transfer of multiple electrons. Photoinduced electron transfer involves reactants in the excited state and therefore differs from both the homogeneous thermal and the electrochemical heterogeneous cases. Pulse radiolysis is different again in the sense that it generates solvated electrons and strong oxidizing and reducing agents, and the ET initiation is usually subject to a large standard free energy. An aspect where these initiation modes do not present the same value is ET-initiated organic synthesis. It is nevertheless possible, when all these factors are taken into consideration, to acquire complementary information regarding the nature of the ET process and its kinetics with respect to the chemical step that follows through use of different initiation modes.

The techniques related to these different initiation modes have been extensively covered in previously published reports, so we briefly review some of the most commonly used methodologies. Their importance in relation to ET processes and associated bond cleavage and bond formation reactions will be discussed in the following chapters. Examples regarding the determination of important kinetic and thermodynamic parameters as well as the investigation of the reaction mechanisms will be presented.

In order to clarify the expected parameters and information to be gained about ET-initiated reactions from the different techniques, the most generally encountered pathways as shown in Scheme 12 will be discussed. The reactant is assumed to be neutral, and a reduction is given as an example. Application to non-neutral reactants and for oxidative processes can be readily achieved through extrapolation and changed charges. One can therefore view an initial electron transfer (reaction 1) as a potential trigger for four main processes: bond cleavage (reaction 2), bond formation (reactions 3 and 4), an additional ET (reaction 5) or a rearrangement (reaction 6). In the case of a bond cleavage-initiated ET, two main mechanisms need to be considered. The initial electron transfer can occur simultaneously with the bond dissociation (reaction 1′) and is referred to as a concerted DET. The bond cleavage can also take place as a separate step following the initial ET. This process is referred to as stepwise DET. The first important question when investigating DET-initiated reactions is therefore to determine whether the first ET and bond breaking are concerted or successive steps. The variety of techniques that provide information about the first ET step as well as subsequent chemical and ET steps are intrinsically related to the different ET initiation modes.

## 3.1. Electrochemical Initiation and Related Methodologies

In electrochemistry, ET between an electrode and a reactant in solution is induced through the application of a specific potential or current to the electrode. The ability to control the electrode potential and/or current is a very important aspect of electrochemical techniques especially because, while one of these parameters is being varied, the other can be simultaneously measured. This makes it possible to both alter and monitor the dynamics of the induced reactions at the same time. The current−potential relationship in electrochemistry is relevant because its analysis provides information about the mechanism, energetics and kinetics of the different steps, including both ET and associated homogeneous chemical steps. In addition, the facile coupling of spectroscopic techniques to electrochemistry provides additional information regarding the processes through characterization and monitoring of both the reactive intermediates and products: electrochemically-generated intermediates can be identified and their kinetics unraveled through their spectroscopic characteristics.

The principles of electrochemical techniques can be found in the extensive literature available.[181−185,225,226]

### *3.1.1. Linear and cyclic voltammetry*

Cyclic voltammetry (CV) is among the most widely used methods for the investigation of ET reaction dynamics and mechanisms.[181−185,225−227] In addition to the general advantages described above, cyclic voltammetry possesses two additional assets: one is the ability to vary the working electrode potential linearly with time, and the other is that this variation can be changed over a wide range of scan rates going from a few mV/s to a few MV/s. In a linear sweep voltammetric experiment, the potential of the working electrode is varied linearly with time, relative to a reference electrode, between two limiting values and the current at that same electrode is measured. In cyclic voltammetry, a second scan is performed to bring the working electrode potential back to its initial value. The different parameters needed to understand the dynamics and mechanisms of ET-initiated reactions can thus be determined. In addition, depending on the nature of the ET reaction and its kinetics compared to those of the coupled chemical reaction comparisons can be made. Thermodynamic parameters such as standard reduction or oxidation potentials ($E°$) can be directly measured if the one electron transfer product is stable enough to be detected. With normal (millimeter diameter) electrodes, standard potentials can be determined for ET products with lifetimes of the order of tens of milliseconds or greater. This limit can be pushed to the microsecond range through use of ultramicroelectrodes and very high scan rates.[228−244] From a kinetic point of view, CV can be used to measure, either directly or indirectly, the rate constants of ET reactions as well as those of coupled chemical reactions. This depends on whether the ET is outer-sphere or inner-sphere in nature and on its kinetics. Another important parameter that can readily be determined using CV is the number of electrons exchanged in the overall reaction. The transfer coefficient is also of great importance especially when the ET is a slow process as will be discussed later. The variation of the peak potential with the scan rate also provides important insights into the reaction kinetics and mechanism.[245−250]

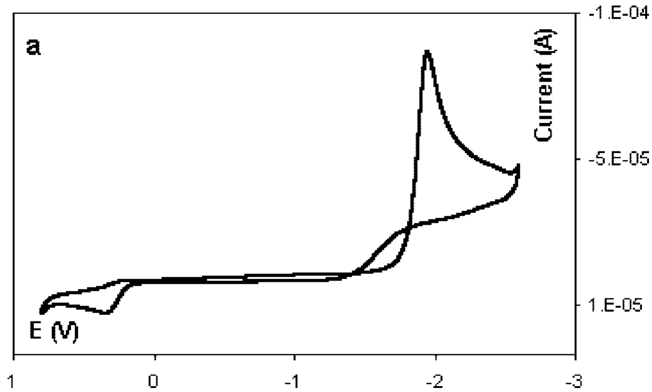
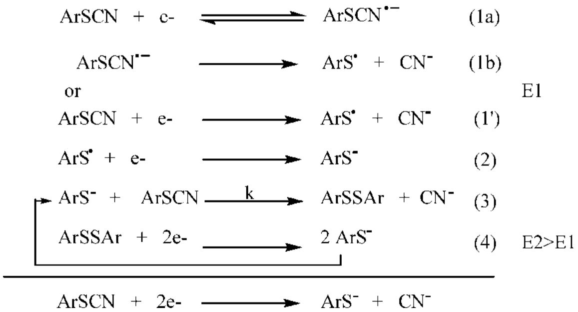



**Figure 1.** Cyclic voltammetry in $CH_3CN$/tetrabutylammonium tetrafluoroborate (TBAF) (0.1 M) at a glassy carbon electrode, $v$ = 0.2 V/s, temperature = 20 °C of 4-$CH_3PhSCN$ (3.26 mM). Adapted with permission from ref 30. Copyright 2003 American Chemical Society.

The importance of CV is that different mechanistic pathways can be identified based on these specific parameters and on their dependence on a number of variables such as the concentration of the reactants, the scan rate, the pH and the temperature. The expected cyclic voltammetric behavior for a wide variety of ET-initiated mechanisms is well described in the literature.[181−185,225−227] It is also possible to unravel novel and unusual mechanisms using CV. One interesting example in this context is the reduction of aromatic thiocyanates.[30] A typical cyclic voltammogram for this series, corresponding to the reduction of 4-methylphenyl thiocyanate, is shown in Figure 1. The cyclic voltammogram shows a very sharp reduction peak, and trace crossing is observed when the scan direction is reversed. The 4-methylphenyl thiolate is generated through a reductive process and can readily be identified by its oxidation peak observed when the potential is scanned toward more positive values. Through analysis of the voltammetric behavior as a function of the scan rate and the thiocyanate concentration, an interesting autocatalytic process (Scheme 13) has been revealed. The uniqueness of this mechanism is that a two electron reduction of the aryl thiocyanate leads to the thiolate, which then reacts with the parent structure through a nucleophilic substitution (reaction 3) to yield the corresponding disulfide. The latter is easier to reduce than the starting material, and its reduction generates more thiolate. The thiocyanate is therefore consumed competitively by both electrochemical reduction at the electrode and nucleophilic substitution in solution. A set of dimensionless partial

**Scheme 13. Mechanism of Electrochemical Reduction of Aryl Thiocyanates**




derivative equations, initial and boundary conditions have been used to describe the mechanism depicted in Scheme 13. This led to a kinetic dimensionless parameter ($\lambda = RTkC°/Fv$) which represents a measure of the competition between the rate determining step of the autocatalytic process (reaction 3) and diffusion. Analysis showed that the electrochemical reduction should predominate at lower thiocyanate concentrations and high scan rates and that the nucleophilic substitution should predominate at higher concentrations and lower scan rates. This was readily verified using CV by monitoring the shape (appearance and disappearance of crossing) and the characteristics (peak potential, peak current, peak width and transfer coefficient) of the reduction peak as a function of the thiocyanate concentration and the scan rate (see Figure 2).

### 3.1.2. Homogeneous Redox Catalysis

In homogeneous redox catalysis, the substrate is reduced or oxidized by an electrochemically generated intermediate Q. Again taking the reduction of a reactant RX as an illustration, the mediator couple (P/Q) is chosen so that its reduction is reversible and fast and is easier than that of the investigated substrate (Scheme 14). The homogeneous ET between Q and the reactant results in an increase of the cathodic current, associated with ET between the electrode and P, and a consequent decrease of the anodic current. This is associated with the ET between Q and the electrode, since Q is now consumed in solution until a complete loss of reversibility is observed (Figure 3).[181,251–260] The variation of the ratio ($i_p/i_0$), of the catalytic peak current ($i_p$) and the peak current of the mediator P in the absence of the reactant ($i_0$), is an important parameter. Its variation with the scan rate and the reactant to mediator concentration ratio ($\gamma = C_{reactant}/C_P$) provides crucial information regarding the kinetics of the involved process.

Homogeneous catalysis is particularly useful for ET processes followed by subsequent chemical steps. It allows the detection of intermediates with lifetimes up to a nanosecond which cannot be detected using direct electrochemistry. If the ET is the rate limiting step, i.e. the following chemical reaction is faster that the ET return including the concerted process, then only the homogeneous electron transfer rate constant between Q and the reactant, RX can readily be determined. No information on the kinetics of the subsequent chemical step can be derived. If the chemical step is the rate limiting step, one can determine its rate constant if the equilibrium constant ($K$) between the reactant RX and the mediator Q (Scheme 14) is known. This can be determined from their respective redox potentials. Even in intermediate cases where the reaction is under mixed kinetic control, both the homogenous ET rate constant and the chemical step rate constant can be determined.[261–265] Since it is possible to vary the free energy of the reaction by changing the P/Q couple, the rate constant of the homogeneous electron transfer can therefore be determined as a function of the standard free energy of the reaction.

Homogeneous redox catalysis can also provide information about the standard potential. When the subsequent chemical reaction is too fast, i.e. ET is the rate limiting step, analysis of the (forward) homogeneous ET rate constant as a function of the standard potential of the mediator may be used efficiently to derive the standard redox potential of the reactant if the activation energy is not too high.[254,266,267]

Interestingly, the interpretation of the CV behavior and deduction of valuable parameters in homogeneous redox catalysis can be straightforward even in the case of mechanisms involving a multitude of associated chemical reactions. This is the case, for example, for electron catalytic mechanisms such as the $S_{RN}1$ reaction (Scheme 2)[268–271] or in reactions where the ET step is preceded by a chemical equilibrium.[272,273] In the latter case, a very recent example has been encountered in the reduction of xanthylideneanthrone and thioxanthylideneanthrone.[273] In this case both A and A′ are reduced by the mediator as shown in Scheme 15. Even if the equilibrium is largely in favor of the reactant A and only a very small amount of A′ exists initially, the homogeneous redox catalysis of the latter has been shown to have an important impact on the system's behavior because the electron transfer to A′ is faster than that to A.

For $S_{RN}1$ reactions, homogeneous catalysis has been shown to be of particular interest when the intermediate radical anion of the initial substrate cleaves very fast or when the initial ET and the bond dissociation are concerted. Under such conditions, the reduction of the intermediate radical is inevitable when direct electrochemical reduction is used to initiate the $S_{RN}1$ reaction. An efficient alternative is, therefore, the use of homogeneous redox catalysis (Scheme 16). Here the nucleophilic attack of the intermediate radical is more favorable since the reduction of the radical at the electrode surface is limited under these conditions because it is generated in solution far from the electrode surface and only its reduction by the mediator competes with the nucleophilic attack.

For a complete review of redox homogeneous catalysis the reader may refer to the literature.[181–185,225,226]

### 3.1.3. Convolution Analysis

Convolution analysis was initially reported many years ago[274–277] and has been used rigorously to explore reaction mechanisms and to unravel valuable kinetic and thermodynamic data for several systems.[30,31,48,51,83,278–281] An important advantage is that all data points of the voltammetric curve are used in the kinetic analysis and that no assumptions on the ET rate law are made in the analysis of the experimental data. This differs from the conventional voltammetric method where a linear activation−standard free energy relationship is implicitly assumed.[183,226,244] An interesting feature of convolution analysis, in the current context, is that it allows determination of the heterogeneous electron transfer rate constant, the activation energy of the reaction and the transfer coefficient as a function of the potential along a cyclic voltammetric peak.

The analysis proceeds as follows: the background-subtracted voltammograms are convoluted to yield convo-

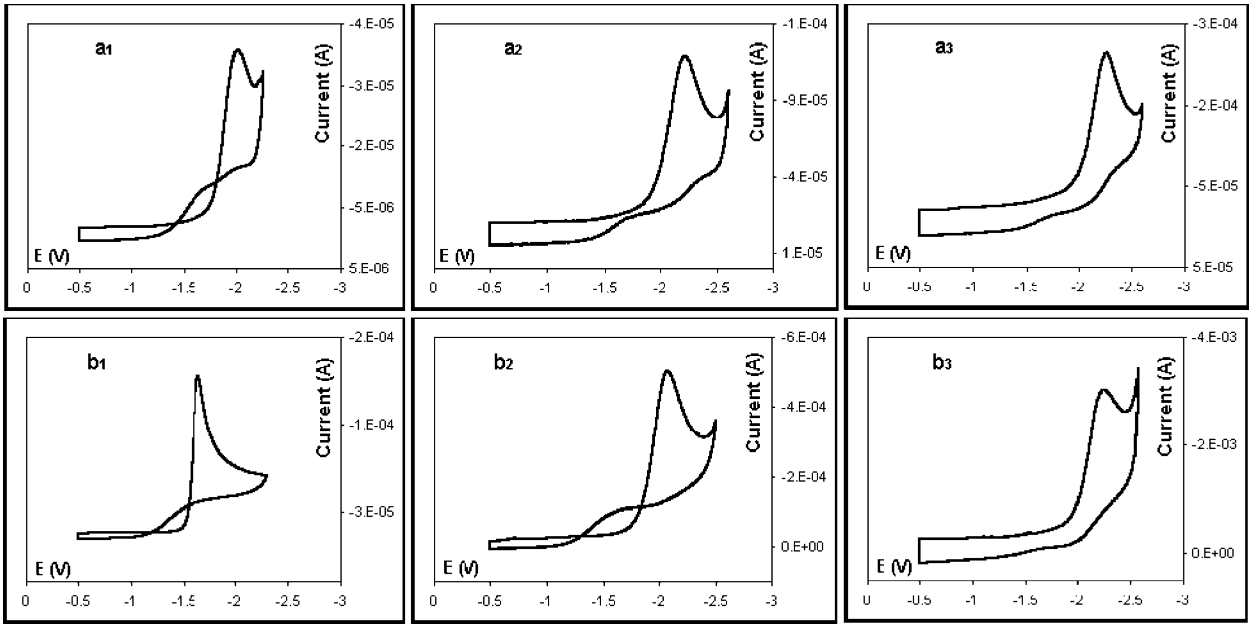
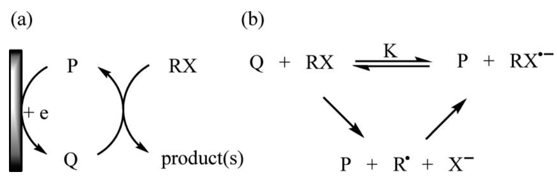



**Figure 2.** Cyclic voltammetry of 4-methylphenyl thiocyanate: ($a_1$) 0.85 mM, 0.2 V/s; ($a_2$) 0.85 mM, 2.4 V/s; ($a_3$) 0.85 mM, 7.2 V/s; ($b_1$) 5 mM, 0.2 V/s; ($b_2$) 5 mM, 2.4 V/s; ($b_3$) 5 mM, 60 V/s. In $CH_3CN$/TBAF (0.1 M) at a glassy carbon electrode. Temperature = 20 °C. Reprinted with permission from ref 30. Copyright 2003 American Chemical Society.

**Scheme 14. Homogeneous Redox Catalysis: (a) General Process at Electrode and (b) Reaction Sequence for a Homogeneous Dissociative Electron Transfer Reduction**



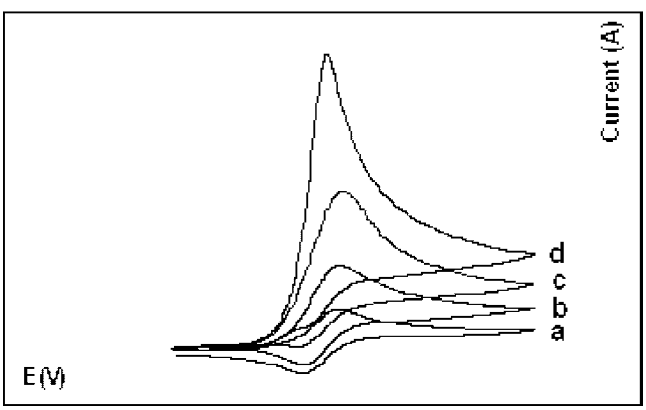
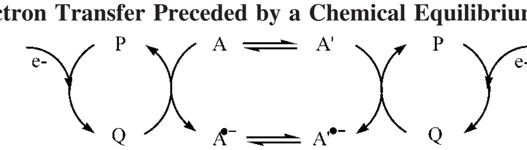
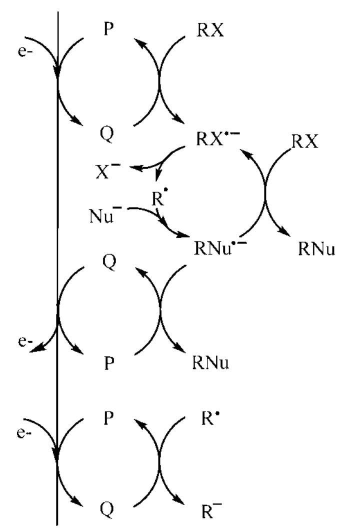




**Figure 3.** Cyclic voltammetry of the mediator P/Q couple in the absence (a) and presence of increasing concentrations (b to d) of the substrate RX.

**Scheme 15. Homogeneous Redox Catalysis for a Reductive Electron Transfer Preceded by a Chemical Equilibrium**




**Scheme 16. Homogeneous Redox Catalysis Mechanism for the $S_{RN}1$ Reaction**




luted current $I$ vs $E$ plots (Figure 4). $I$ is related to the voltammetric current $i$ through the convolution integral (eq 1).

$$I = \pi^{-1/2}\int_0^t \frac{i(u)}{(t-u)^{1/2}}\,\mathrm{d}u \tag{1}$$

The limiting current $I_l$ is defined as $I_l = nFAD^{1/2}C^0$, where n is the overall electron consumption per molecule, A the electrode area, $D$ the diffusion coefficient of the reactant, and $C$ its bulk concentration. $I_l$ is independent of scan rate and can be used to calculate $D$, knowing the area of the working electrode and the number of electrons consumed in the electrochemical process.

Although the technique is applicable to different electron transfer mechanisms, it has been found to be particularly important for totally irreversible systems. This is when the dissociation is very fast or the mechanism is concerted where kinetic and thermodynamic data are less readily accessible. Under these conditions $I_l$ can be related to the rate constant of the heterogeneous electron transfer $k_{het}$ through eq 2. Systems following a single ET mechanism show either a linear or a parabolic pattern.

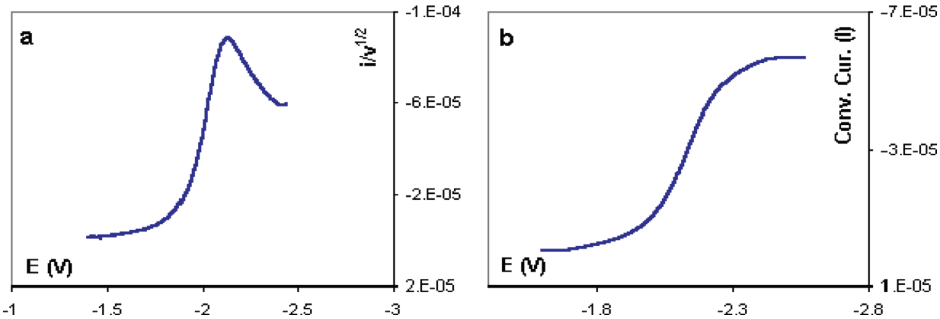



**Figure 4.** (a) Background subtracted linear voltammogram and (b) variation of convolutive current with potential for *p*-methoxyphenyl thiocyanate (0.69 mM) in $CH_3CN$/TBAF (0.1M) at $v$ = 20 V/s, temperature = 20 °C.

$$\ln k_{het} = \ln D^{1/2} - \ln \frac{I_1 - I(t)}{i(t)} \tag{2}$$

A wealth of important data can thus be gained through application of the convolution analysis. A particularly interesting aspect of convolution analysis is its ability to provide evidence for electron transfer processes where both mechanisms are involved (see section 5.1).

### *3.1.4. Electrochemical Determination of Redox Properties of Transient Radicals*

The importance of the redox properties of intermediate transient species such as radicals is two-fold. The first is fundamental as the redox properties of intermediate radicals can provide insights into the mechanisms involved (radicalar vs ionic).[282–284] These can be used in thermodynamic cycles to obtain crucial parameters such as bond dissociation energies, standard redox potentials, $pK_a$ values and others.[285–287] The second is practical since these radicals may create applications in electron transfer initiated synthesis[2–5] or for the modification of conducting[85–87,89–93,288–291] and semi-conducting[88,292–294] solid surfaces. Different methods and approaches have been developed for the determination of the redox potentials of radicals.[295]

Except in rare cases such as in the reduction of diazonium salts, radicals generated through electron transfer are usually easier to reduce (or oxidize) than their corresponding starting materials and are therefore immediately reduced (or oxidized) under electrochemical conditions. In cyclic voltammetry for example, the radical is usually reduced or oxidized at the same peak as the starting material and it is very rare that a distinct peak is observed for an intermediate radical.[70,190,296,297] The deduction of the standard redox potentials, in the thermodynamic sense, of these radicals (from the corresponding peak potentials) has been achieved through analysis of the voltammetric peak. It is necessary to take into consideration the thermodynamic (standard redox potentials) and kinetic (rate constants of the electron transfer, follow-up chemical reaction, and diffusion of the species in solution) parameters. In certain cases, the redox potentials of radicals can also be obtained through the electrochemical investigation of the corresponding anions and/or cations.[298–317] An estimation of the redox properties of transient radicals can also be obtained through the use of homogeneous catalysis.[257,259,318–322]

Other techniques have also been developed in order to investigate the redox properties of radicals usually generated through photochemical irradiation.[323–328] A very interesting technique is photomodulation voltammetry. Here radicals are generated by irradiation of a solution with modulated light, and their redox properties are obtained by monitoring the in-phase current−potential variation. Usually a gold mesh is used as the working electrode although a small microdisk electrode has also been used.[329] The solution may contain the precursor if direct irradiation can lead to the desired radical; otherwise a radical initiator is added and the radical is obtained indirectly. Both the precursor and the radical initiator should be more difficult to reduce (or oxidize) than the generated radical. Half-wave potentials for a wide variety of radicals both in reduction and oxidation have thus been determined.[330–339]

Another technique that has proven very useful in obtaining reduction potentials of radicals is laser flash electron injection.[340–343] In this technique the reactant is reduced through capture of photoejected electrons from a laser-irradiated electrode. The reactant is therefore insensitive to the laser pulse and the generated radical is investigated at the same electrode. The radical can be reduced either at the same electrode, when the applied dc potential allows it, or in solution. A radical reduction polarogram-type graph is obtained reflecting the photoinjected charge as a function of the dc potential of the electrode thus allowing a half-wave potential to be obtained. This parameter contains both thermodynamic and kinetic information regarding the electron transfer to the radical, as well as potential subsequent chemical reactions. A methodology for obtaining the corresponding standard reduction potential as well as thermodynamic and kinetic parameters has also been reported.[344]

### *3.1.5. Spectroelectrochemistry*

Electrochemical methods have been also successfully coupled to different spectroscopy techniques extending capabilities and the possibility of gathering additional information mainly regarding characterization and kinetics of the intermediates involved.[345–347] Different configurations have been developed and applied to a variety of ET reactions based on their kinetics, the stability of the transient intermediates generated and the physical properties of both intermediates and products.[184] The spectroscopic methods employed include ESR,[348] NMR,[349–351] mass spectrometry,[352–354] and optical spectroscopy.[355] Unlike other techniques such as laser flash photolysis and pulse radiolysis which also rely on spectroscopy, spectroelectrochemical techniques often have the advantage of being particularly complementary to techniques such as CV. Since the initiation mode is identical, similar chemical processes usually take place and can be monitored by the spectroscopic characteristics of the reactants, intermediates and/or products.

Due to its relative simplicity optical spectroscopy is the most frequently used methodology. In addition, a large range of ET-initiated processes for different types of reactants can readily be monitored through their optical properties. Many examples can be found in the literature.[345] While both UV−vis and IR[356] spectroscopies have been combined with electrochemical techniques, the former has been more widely applied mainly due to the complications associated with the sensitivity of IR.[357] Different configurations have been designed for both UV−vis and IR[358–360] detection techniques. The former has been used for the determination of the formal redox potentials and the numbers of exchanged electrons for a variety of inorganic ions and enzymes.[345,361] IR spectroscopy used in combination with a stop flow system has been used to study ET-based reactions.[362,363]

An important aspect of ESR[364] which is particularly useful for the investigation of radicals, radical ions and certain transition metals is its great sensitivity (as low as $10^{-8}$ M). Coupled with electrochemical techniques it has been used to investigate electrochemically generated intermediates using different configurations.[365–370] Radical intermediates can be detected either directly or through the use of spin traps.[371,372] Valuable information regarding intermediates, their kinetics and interactions with their surrounding is obtainable.[373]

Due to the importance of nuclear magnetic resonance (NMR) as a powerful tool for structural characterization in chemistry, understandably the coupling of NMR and electrochemistry to monitor electron transfer reactions has been the focus of some attention. This has led initially to different designs where NMR was used only as an *ex situ* technique.[374–377] More recently, it has been shown that it is also possible to characterize *in situ* electrochemically generated products in solution.[351] Excellent resolution was obtained when the electrochemical reduction of *p*-quinone in deuterated water under acidic conditions was monitored.[351] There are an increasing number of applications where the *in situ* NMR characterization under electrochemical conditions is proving useful especially in battery research.[378,379]

Mass spectrometry is another technique that has been successfully coupled with electrochemistry.[380] Although the initial configuration, designed to detect electrochemically generated volatile products, had a significant time delay (response time for detection: 20 s), real-time analysis during a potential scan is now possible.[381–383] Further improvement allowed analysis of the electrolytic solution through vaporization of the solution using a heater.[352,384–386] An interesting example using this mass spectrometry−electrochemistry coupling is the electrochemical oxidation of the potent neurotoxin, 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (MPTP) and some closely related derivatives. These have been shown to induce symptoms of Parkinson's disease.[387] The reactive pathways of electrochemically-generated intermediates have also been monitored through the successful coupling of an electrochemical cell to a mass spectrometer.[388,389]

## 3.2. Photochemical Initiation

Photochemical irradiation is another efficient way to initiate ET reactions. Many processes in nature are based on photoinduced ET. The most widely known one is of course photosynthesis. Under photochemical irradiation the ET can occur through a variety of mechanisms (shown in Scheme 17): from irradiation of the donor (i) or of the acceptor (ii).[390,391] It is also possible to generate solvated electrons, through irradiation of a sensitizer that is trapped by an acceptor (iii).[392,393] Electron photoejection has been reported for anions such as phenolates and thiolates as well

**Scheme 17. Different Mechanisms for the Photochemical Initiation of a Dissociative Electron Transfer**

(i)
$$D \xrightarrow{h\nu} D^*$$
$$D^* + RX \longrightarrow D^{\bullet+} + R^{\bullet} + X^-$$

(ii)
$$RX \xrightarrow{h\nu} RX^*$$
$$D + RX^* \longrightarrow D^{\bullet+} + R^{\bullet} + X^-$$

(iii)
$$D \underset{}{\overset{h\nu}{\rightleftharpoons}} D^{\bullet+} + e^-$$
$$RX + e^- \longrightarrow D^{\bullet+} + R^{\bullet} + X^-$$

(iv)
$$D + RX \longrightarrow (D,RX) \xrightarrow{h\nu} D^{\bullet+} + R^{\bullet} + X^-$$

as for neutral structures such as 4,4′-dimethoxystilbene.[392,393] This latter process is similar to pulse radiolysis. A charge transfer complex may also be formed: either before irradiation between ground state reactants or after irradiation between excited and ground state structures (iv).[394–396] Of the different techniques that have been developed to study photoinduced electron transfer reactions[397] the most widely used one is laser flash photolysis.

### 3.2.1. Laser Flash Photolysis

This is the method of choice for the investigation of the kinetics of photoassisted ET reactions. It is a powerful technique used to study transient intermediates such as those generated in ET reactions including radicals, ions and radical ions.[398] The methodology originates from the flash photolysis technique developed by the Nobel Prize winners Porter and Norrish who used a flash lamp to produce the light pulse.[399–402] It was capable of studying reactive intermediates with multimicrosecond resolution. This capability was extended to nanosecond resolution through the introduction of a laser as light pulse source.[403] Further technical progress was made through the introduction of computers for experimental control as well as data acquisition and analysis. Technical advances in the development of ultrafast powerful pulsed lasers, higher resolution detection systems and high-speed computers led to even faster systems with time domain detection currently in the femtosecond range.[404] In laser flash photolysis, the irradiated solution containing the donor and acceptor is monitored through the variance of its absorbance in the UV−vis or IR regions.[405] Some difficulties associated with laser flash photolysis that need to be taken into consideration are the adequate choice of the initiation mechanism and appropriate reactants. The tendency of certain reactions to regenerate the initial reactants through back electron transfer must also be taken into account.[405–407] The potential overlap of the reagent absorptions may trigger undesirable reactions, and their overlap with the intermediates could further compromise the ability to detect them and study their kinetics.

## 3.3. Initiation by Solvated Electrons

Solvated electrons present another method for the initiation of ET reactions. Easily oxidizable metals such as sodium, potassium and lithium are extensively used in chemistry in reduction processes. One interesting and relevant example is the Birch reduction where an aromatic ring is reduced.[408–411]

**Scheme 18. Water Radiation Reactions**

$$H_2O \rightsquigarrow H_2O^* \longrightarrow H^\bullet + {}^\bullet OH \quad \text{or} \quad H_2 + O(^1D)$$

$$H_2O \rightsquigarrow H_2O^{\bullet +} + e^-$$

$$H_2O^{\bullet +} + H_2O \longrightarrow H_3O^+ + {}^\bullet OH$$

$$e^- + nH_2O \longrightarrow e^-_{aq}$$

$$2\,HO^\bullet \longrightarrow H_2O_2$$

### 3.3.1. Pulse Radiolysis

Pulse radiolysis is another technique that allows the generation of similar strong oxidizing and reducing agents. In addition, it provides kinetic and mechanistic information. Since its initial introduction[412–414] it has been recognized as an efficient technique for the investigation of ET processes[415,416] since it allows both the detection of transient intermediates and investigation of their kinetics. This technique relies on the generation of strong reducing and/or oxidizing intermediates through exposure of a solvent to high-energy flux radiation either in the absence or in the presence of specific agents. These intermediates are usually monitored through their optical properties. Older detection methods such as conductivity,[415] polarography,[417] NMR,[418] EPR,[419] Raman scattering[420] and microwave absorption[421] have been less frequently used. The pressure and the temperature can be controlled in pulse radiolysis experiments.[416] Although water has been the most widely employed solvent, many other organic solvents including alcohols, acetonitrile, ammonia, acetone, chlorinated hydrocarbons, dimethylsulfoxide, cyclohexane, 2-methyltetrahydrofuran and 2,2,4-trimethylpentane as well as mixtures of organic solvents have all been used.[416,422] Systems with ultrafast pulses have also been used for the investigation of even faster chemical reactions.[423,424]

In the case of water, low linear energy transfer radiation[416] causes both excitation and ionization of the water molecules. This leads to the initiation, therefore, of a series of fast reactions (Scheme 18) generating intermediates with powerful reducing (solvated electron and hydrogen radical) and oxidizing (hydroxyl radical) abilities.[416,425] The addition of specific agents converts some of these intermediates to the more desirable “totally” reducing or oxidizing conditions.[416] Quenching of the solvated electrons using $N_2O$ has been found to be a convenient way to study oxidation processes[416] since it allows the generation of hydroxyl rather than hydrogen radicals in large excess. To investigate reductive processes, solvated electrons can be used as the reducing agent, but in this case hydroxyl radicals are quenched and converted to other “unreactive radicals”.[416] Other strategies can be used such as converting all the main intermediates (e-, H and OH) to the same reducing agent through reaction with acetone or an alcohol such as methanol, ethanol or 2-propanol[426] in the presence of $N_2O$.

## 3.4. Thermal Homogeneous Electron Transfer

Electron transfer may also take place spontaneously after mixing two reactants if the reaction thermodynamics allow it: if the standard Gibbs energy ($\Delta G°$) is negative or if a fast chemical reaction follows. Under these conditions the ET between a donor (D) and a reactant RX takes places in solution as shown in Scheme 19. The relevance of studying homogeneous ET is dictated by its importance in a wide variety of natural processes as well as its omnipresence in synthesis through the use of oxidizing and reducing agents.

Different techniques have been developed to measure the rate constants of homogeneous ET reactions. These include a range of mixing methods that are continuously being improved as well as related detection methods that can monitor the reactants, products or transient intermediates.

### 3.4.1. Self-Exchange Electron Transfer

These reactions are unusual in that the reactants and products are identical and hence the physical properties of the system before and after ET remain the same. Self-exchange reactions using transition metals were intensively used for the testing of the fundamental aspects of ET theories.[427–429] For an exhaustive report the reader is referred to an excellent recent review by Swaddle.[430]

The investigation of self-exchange electron transfer reactions is traditionally achieved through periodic quenching of the products through the use of molecular traps followed by separation and analysis to quantify the products and hence determine the rate constants. This methodology has been extensively applied to kinetic studies[431,432] as well as the formation of the precursor complex structure preceding the ET step, reorganization energies and electronic coupling. The ET mechanisms both inner vs outer-sphere electron transfer and adiabatic vs nonadiabatic,[433–438] the effect of the solvent and interactions with host molecules,[439–441] have all been explored. These reactions have also been investigated using spectroscopic techniques such as EPR[442] and NMR line-broadening analysis.[443,444]

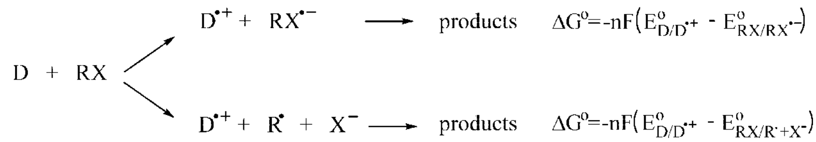
### 3.4.2. Stop Flow

The stop flow methodology has proven of great importance since it provided rate constants that were used in the initial testing of the highly relevant Marcus theory.[445,446] In this technique, two (or more) reactant solutions, in separate syringes, containing a donor and an acceptor respectively, are mixed together just before their introduction into the observation chamber. The reaction can be monitored through absorbance of the reagents, intermediates and/or products in the UV−vis or IR regions[447] or using EPR.[448] It has also been coupled to other techniques such as pulse radiolysis,[449] laser flash photolysis[450] and electrochemistry.[43,46]The shorter the instrument’s dead time and the smaller the pathway length, the higher the rate constants to be detected.

### 3.4.3. Continuous Flow

Here the reactant solutions are continuously flowing through the mixing chamber and into the observation tube where they are detected. In traditional systems both the flow of the reactant solutions and the detection point within the observation tube can be varied to allow kinetic measurements of species with half-lives up to the millisecond. Improvements have limited the need for large volumes of reactant solutions, extending the ability to study even faster processes.[451] One interesting improvement is the incorporation of the mixing and the observation chambers to give a “continuous flow method with integrating observation”. This extends the time resolution by two orders of magnitude.[452]

**Scheme 19. Homogeneous Electron Transfer between a Donor D and an Acceptor RX**



The introduction of pulse instead of a continuous flow[453,454] made it possible to study the kinetics of ET reactions.[453] Continuous flow has also been coupled with stop flow techniques to investigate ET kinetics.[455]

## 4. Electron Transfer Reactions: Fundamental Aspects and Experimental Examples

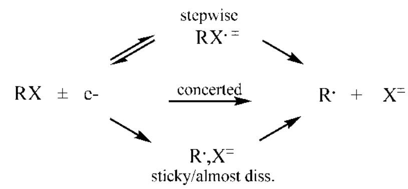
Since ET theories have been the subject of many studies and have been extensively reviewed, only concepts relevant to this review will be presented here. These will serve as the basis for the discussion of various recent findings in the field. Readers interested in the details of electron transfer theories are referred to the many sources and references cited in this section.

As discussed in the previous section, ET reactions are usually associated with a variety of structural changes and/or chemical reactions involving bond making and bond dissociation. Two principal situations need to be considered. When the product of the initial single ET is an intermediate, the outer-sphere ET Hush−Marcus model[456–466] is applicable regardless of the fate of this intermediate. Since it only involves structural changes (bond distances and angles), the intrinsic barrier associated with such an electron transfer is relatively low.

The second scenario is encountered when bond cleavage is associated with the electron transfer. If the ET and the bond cleavage take place in separate steps involving the intermediacy of single ET product, the outer-sphere ET model is still applicable. Otherwise, when the ET and the bond cleavage are concerted (concerted DET) then the outer-sphere ET model can no longer be used to describe this process. Savéant's model,[283,467–469] which is based on the Morse curve picture of bond breaking, must now be used. The intrinsic barrier associated with this DET mechanism is large since it is now associated with the cleavage of a chemical bond.

Intermediate cases, where "modifications" of the existing "classical" theories are needed, have also been reported. An interesting case is when the fragments obtained through a concerted ET mechanism form a radical/ion pair through interactions within the solvent cage. This mechanism is referred to as "sticky" DET. Savéant successfully extended the DET model to take into account the existence of these interactions. The increasing relevance of this mechanism is due to the increasing number of examples of systems found to undergo the sticky DET mechanism. A closely related mechanism is that involving the formation of a "loose" $\sigma$ radical anion intermediate that dissociates very quickly. This mechanism has been referred to as the "almost" DET mechanism. The formation of a less stable radical anion induces an increase in the intrinsic barrier compared to the classical stepwise mechanism. The intrinsic barrier encountered in both these cases is lower than that corresponding to a concerted one, but it is still significantly higher than that corresponding to a stepwise mechanism.[26,60,61,64,470] Conceptually, the two cases can be viewed as only differing in the degree of interaction between the two intermediate moieties. Scheme 20 provides a description of these important pathways, and this section will briefly describe the fundamental aspects associated with them. For these mechanisms, the reaction activation energy depends on both thermodynamic and kinetic factors through a quadratic activation−driving force relationship. This relationship differs from one case to another by the extent of the internal changes within the molecule during the ET process and by the degree of interaction between the fragments generated.

**Scheme 20. Principal Dissociative Electron Transfer Mechanisms**



### 4.1. Outer-Sphere Electron Transfer

Since the early experiments in ET chemistry using self-exchange reactions (isotopic exchange reactions), attention has focused on developing a model that can account for this type of chemistry. The first attempts were oriented toward the modelization of these same self-exchange reactions. Later this was further extended to the case of cross ET reactions, before reaching a more general description which included the case of heterogeneous ET at an electrode.[460]

Most of this ground breaking work was carried out by Marcus and Hush.[456–466] The initial self-exchange formulation assumed a weak electronic interaction of the reactants involved in the ET reaction. The fluctuations of the nuclear coordinates of the entire system, including the solvent molecules, were considered so that both the Franck−Condon and energy conservation principles were satisfied. Initially, the solvent outside the first coordination shell was described in terms of a dielectric continuum approximation.[457,458] Later a purely molecular treatment was used where the solvent molecules were treated as a collection of dipoles.[471,472] Both the solvent and the reactant molecules were treated in terms of a general charge distribution system. This approach permitted depiction of the reaction through free energy plots as a function of a global reaction coordinate (Figure 5).

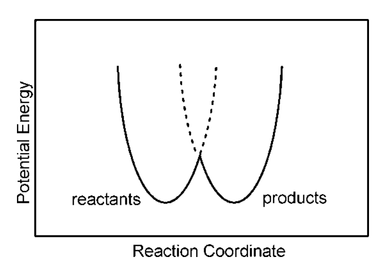



**Figure 5.** Morse curves for an outer-sphere electron transfer at zero driving force.

This intensive research lad to the formulation of the well-known outer-sphere ET theory by Marcus and Hush. This provides a relationship between the activation free energy ($\Delta G^{\ddagger}$) of the reaction and its standard free energy ($\Delta G^{0}$), as depicted in eq 3:

$$\Delta G^{\ddagger} = W_R + \Delta G^{\ddagger}_{0,os}\left(1 + \frac{\Delta G^0 - W_R + W_p}{4\Delta G^{\ddagger}_{0,os}}\right)^2 \quad (3)$$

$\Delta G^{\ddagger}_{0,os}$ is the intrinsic barrier (i.e. the activation energy at zero driving force) for the outer-sphere electron transfer and is related to the reorganization energy ($\lambda$) through eq 4. $W_R$ and $W_p$ represent the work required to bring, respectively, the reactants and the products from infinity to the reacting distance.

$$\Delta G^{\ddagger}_{0,os} = \frac{\lambda}{4} \quad (4)$$

$$\lambda = \lambda_0 + \lambda_i \quad (5)$$

The reorganization energy ($\lambda$), which describes the necessary rearrangement of the reactants and solvent molecules along the electron transfer process, includes two main components: $\lambda_i$, which is a contribution of the inner reorganization energy of the reactants, and $\lambda_0$, the contribution of the solvent reorganization energy (eq 5). $\lambda_i$ and $\lambda_0$ were defined for a homogeneous ET by Marcus through eqs 6 and 7, respectively.

$$\lambda_i = \frac{k_j^R k_j^P}{k_j^R + k_j^P}(q_j^R - q_j^P)^2 \quad (6)$$

$k_j^R$ and $k_j^P$ are the normal mode force constants of the $j$th vibrational coordinate in the reactants and products, respectively, and $q_j^R$-$q_j^P$ are the changes in the bond lengths and angles when going from the reactants to the products.

$$\lambda_0 = e^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \quad (7)$$

where $a_1$ and $a_2$ are the ionic radii corresponding to the donor and acceptor respectively. $R$ is the distance separating the centers of the reactants. $D_{op}$ and $D_s$ are the optical and static dielectric constants of the solvent.

This theory that was originally developed to describe homogeneous ET has been successfully applied to heterogeneous ET at the surface of an electrode. In this case, the solvent reorganization energy is described by Marcus through eq 8.

$$\lambda_{0,el} = \frac{e^2}{2}\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)\left(\frac{1}{a} - \frac{1}{d}\right) \quad (8)$$

Here $a$ is the molecular radius of the electroactive species and $d$ is its distance from the center of its electrical image in the electrode.

Hush suggested a relatively close equation that neglected the image effect based on electrostatic arguments[461] (eq 9).

$$\lambda_{0,el} = \frac{e^2}{2a}\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \quad (9)$$

While for relatively large values of the distance $d$ (larger than 2−3 Å) it has been shown that the image effect can be neglected in the presence of a well-established double layer,[473] the inclusion of an image factor decreases the estimate of the reorganization energy by a factor of 2 for small molecules, for which $d$ is simply taken as approximately $2a$.

The image and double layer effects on the reorganization energy were studied later[474] using kinetic data obtained for aromatic substrates in DMF, and it has been suggested that the two factors tend to cancel each other. The study showed a linear variation of the deduced reorganization energies ($\lambda_{0,el}$) with $1/a$, thus providing an alternative simplified way to estimate $\lambda_{0,el}$ (eq 10), especially for compounds with relatively similar structures.

$$\lambda_{0,el} = 3/a \quad \text{where} \quad a = \frac{a_X(2a_{RX} - a_X)}{a_{RX}} \quad (10)$$

where $a_X$ and $a_{RX}$ are the correpsonding radii of the equivalent spheres of X and RX, respectively.

Many aspects of the outer-sphere electron transfer theory and its predictions have been verified experimentally since its inception. One of the most important predictions of the outer-sphere ET theory is the existence of what Marcus termed the "inverted region". Due to the quadratic nature of the activation-driving force relationship, the reaction activation energy, $\Delta G^{\ddagger}$, is expected to first decrease (normal region) as the standard free energy, $\Delta G°$, value varies from 0 to $-\lambda$, where it vanishes, then increases as $\Delta G°$ moves to more negative values. In other words, eq 3 predicts that a reaction would be subject to deceleration as the reaction becomes more and more exoergonic ($\Delta G° \ll 0$). Although the inverted region attracted considerable attention,[475–487] it was initially challenging to prove experimentally.[488–492] The first convincing example was provided by Miller et al.[477] in the study of pulse radiolysis-initiated intramolecular ET in donor−spacer−acceptor systems. Biphenyl was used as a donor, and the intramolecular ET driving force was varied by changing the acceptor. For this a series of aromatic structures or quinones with different standard reduction potentials was used. Figure 6 presents the variation of the experimental intramolecular electron rate constant ($k_{int}$) as a function of the driving force and shows both predicted normal and inverted regions.

Since then many similar systems have been designed using donors and acceptors with large redox asymmetries and have been shown to involve intramolecular ET in the Marcus inverted region.[493–502] A particularly interesting recent study using polychlorinated triphenyl radical as an acceptor and ferrocene or nanoferrocene as donors[501] showed that the photoinduced intramolecular ET undergoes a transition from the normal to the inverted region on changing the solvent polarity. This strongly affects the reorganization energy $\lambda$ through specific H-bonding interactions. The inverted region was also observed in back electron transfer reactions from photoexcited states.[502–509]

Another interesting aspect related to the outer-sphere ET theory is the well-known "cross-relation" (eq 11). Marcus suggested that for cross-reactions involving outer-sphere electron transfers in solution between a donor and an acceptor, the reorganization energy could approximately be regarded as the sum of the reorganization energies for the corresponding self-exchange reactions.

$$\lambda_{AD} \cong \lambda_{AA} + \lambda_{DD} \quad (11)$$

This leads to the well-known expression relating the cross-reaction rate constant $k_{AD}$, to the equilibrium constant $K_{AD}$ and the self-exchange reactions rates constants $k_{AA}$ and $k_{DD}$ (eq 12). $f_{AD}$, which is close to unity, is a function of the

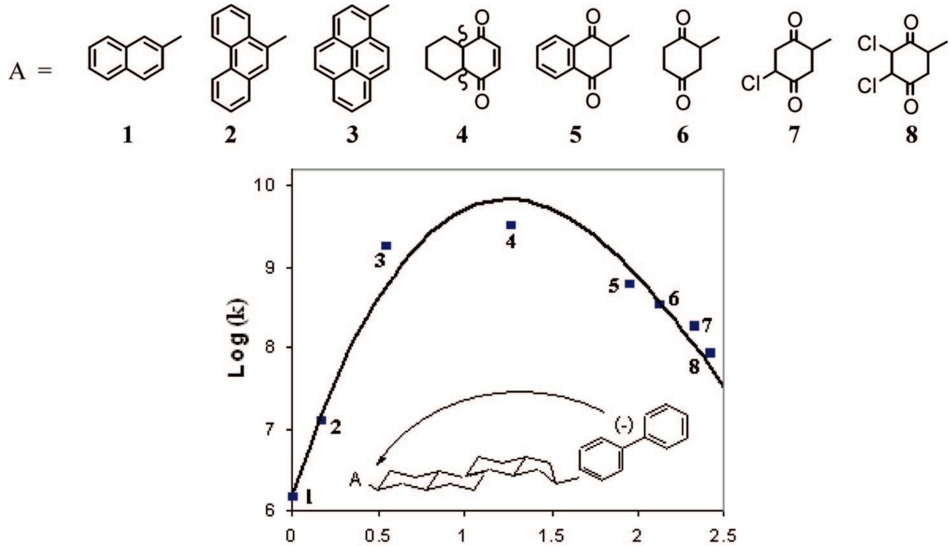



**Figure 6.** Variation of the intramolecular ET rate constant of a series of acceptor−spacer−donor systems as a function of the driving force. Adapted with permission from ref 477. Copyright 1984 American Chemical Society.

latter three parameters.

$$k_{AD} \cong \sqrt{f_{AD} K_{AD} k_{AA} k_{DD}} \tag{12}$$

This equation was successfully applied to large series of inorganic ions for which the experimental and calculated rates constants showed very good agreement.[510]

Other tests of the outer-sphere electron transfer theory came with the increasing abundance of kinetic electron transfer studies. Rate constants were discussed in terms of the two main contributions to the intrinsic barrier, i.e. the internal and the external reorganization energies. An interesting aspect that was known even before the development of the theory was that small inorganic ions undergo slow electron transfer reactions. In the context of the outer-sphere electron transfer theory, this could be understood on the basis of the large external reorganization energy involved. This is due to the strong solvation of these ions by the solvent molecules.[473] Many other examples have been encountered where important internal reorganization has been shown to accompany the electron transfer causing an increase of the intrinsic barrier and hence decreasing the rate constant of the reaction.[210,212,214,219,222,223,511–513] Large aromatic compounds, in contrast, showed rater faster kinetics.[228,464,514] Since the one ET product for these compounds is usually generated either as a stable product or as an intermediate, they are also regarded in the context of the outer-sphere electron transfer theory. In this case small reorganization energies are expected since the electron transfer to or from the aromatic ring does not involve much internal reorganization. Since the structure is large, the solvent reorganization is small.

## 4.2. Adiabacity/Nonadiabacity

The outer-sphere electron transfer model is based on the intersection of two diabatic potential surfaces and therefore assumes strong electronic interaction of the two states at this intersection. The ET depends on the extent of the electron coupling that causes a splitting at the transition states. The Landau−Zener model[515,516] has been successfully used to obtain the probability of the passage from reactants to products (eq 13).[429,517] $H$ represents the energy of the electronic coupling. This leads to the introduction of the electronic transmission coefficient, $\kappa_{el}$, which is related to the probability through eq 14.

$$P^{\ddagger} = 1 - \exp\left(-\frac{H^2}{\lambda_t^{1/2}}\left(\frac{\pi F}{RT}\right)^{3/2}\right) \tag{13}$$

$$\kappa_{el} = \frac{2P^{\ddagger}}{1 + P^{\ddagger}} \tag{14}$$

When the electronic coupling ($\kappa_{el}$) is large, the reaction probability reaches unity and the reaction is termed adiabatic. The resonance energy (avoided crossing) is in many cases large enough to ensure adiabacity but is still, however, considered negligible compared to the activation energy derived from the crossing of the hypersurfaces.

The rate constant of the electron transfer reaction is given by the general expression (eq 15):

$$k = Z\kappa_{el} \exp(-F\Delta G^{\ddagger}/RT) \tag{15}$$

where for an adiabatic electron transfer, $Z$ is the nuclear frequency factor ($Z = k_BT/h$ or $Z = (RT/2\pi M)^{1/2}$) and for nonadiabatic processes $Z$ is an electron hopping frequency ($\nu = 4\pi^2H^2/[h\sqrt{(4\pi\lambda k_BT)}]$).

On the other hand, when $H$ is small, i.e. lower than $RT$ (0.592 kcal/mol),[429] the reaction is termed nonadiabatic and eq 14 can be simplified through development of the exponential to first order to give

$$\kappa_{el} = \frac{2H^2}{\lambda_t^{1/2}}\left(\frac{\pi F}{RT}\right)^{3/2} \tag{16}$$

Most of the relevant available examples involve ET through large distances.[518] These include donors and acceptors separated by molecular spacers and ET at long chain-modified electrodes.[519–528] The electronic coupling distance dependence has been extensively investigated.[428]

Other examples have been shown to involve a high degree of nonadiabicity as found in the reduction of dialkyl peroxides,[47,51] endoperoxides[529] and peresters.[280,281] In such cases the ET has been shown to involve weak electronic coupling based on the nonadiabatic ET model developed by

German and Kuznetsov.[530–533] Estimation of the electronic coupling is generally a complicated issue to which extensive research has been devoted.[439,534–539]

The variation of the interaction energy with the transmission coefficient and the transition between adiabatic and nonadiabatic electron transfer modes have all been investigated.[540,541]

## 4.3. Dissociative Electron Transfer Model

Particular interest has focused on understanding dissociative electron transfer (DET) processes.[185,283,467–469,542] Here a chemical bond is broken as a result of an ET either to or from an organic or bioorganic molecule. As discussed earlier, two main mechanisms need to be considered: one is concerted, where ET and bond breaking are simultaneous, and the other is stepwise where the process involves successive steps. Although the outer-sphere ET theory can successfully describe the latter case, it cannot, however, account for concerted ET reactions. Here where the electron transfer step and the bond breaking are simultaneous, the dynamics of the process, its occurrence and the factors controlling it have all been the subject of intensive research. A considerable amount of work had accumulated over many decades[543] even before the actual DET theory was developed by Savéant. These studies go back as far as the 1930s to the early extensive work by Polanyi on ET to organic halides from alkali metal atoms in the gas phase.[544,545] These have been of great value in testing the predictions of the transition state theory, and in rationalizing the initial electrochemical investigations. Interest in the electrochemical reduction of organic halides also goes back to the late 1940s when ET from a mercury electrode in a mixture of dioxane and water was studied.[546] It is essential to note the pioneering fundamental work of Evans and Hush on the development of an approach for the extraction of rate constants for irreversible ET reactions. They addressed reactions that initially concerned heterogeneous ET to organic halides and carboxylates. The immediate product was viewed as a compressed radical−halide ion pair. This mechanism has only recently been confirmed and modeled and will be discussed in section 4.4.[547,548] Subsequent important contributions were made by Eberson,[549] who later took a different approach toward elucidating the relationship between the ET rate constant and the driving force using the Marcus theory.[550–553] The actual DET that was developed by Savéant provides an effective tool for describing the dynamics of such processes.[467–469]

Savéant suggested a model for thermal concerted dissociative electron transfer processes based on a Morse curve approximation. This approach describes the energy of the cleaving bond in the reactants in terms of a Morse potential curve. It assumes that the repulsive interaction of the products formed following ET is the same as the dissociative component of the reactant Morse curve (Figure 7).

The involvement of the solvent is treated in a similar fashion as the outer-sphere ET model. The ET takes place in the transition state between the two hypersurfaces in agreement with the activation complex theory. This leads to a quadratic activation free energy−driving force relationship similar to that found for outer-sphere ET (eq 17). $\Delta G^{\neq}$ is the activation free energy, and $\Delta G°$ the driving force. The only difference is the contribution, for a concerted ET mechanism, of the bond dissociation energy ($D_R$) of the cleaving bond to the activation barrier (eq 18). This involves only the inner ($\lambda_i$) and the solvent ($\lambda_0$) reorganization energies for a stepwise mechanism (eqs 6 and 7–9).

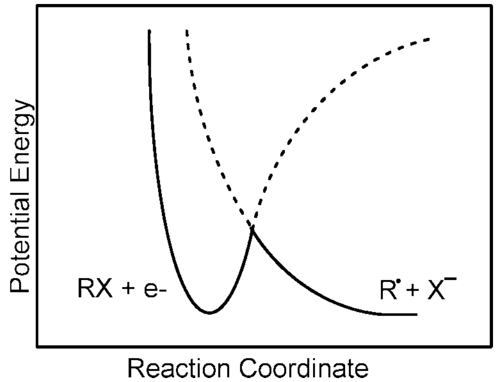
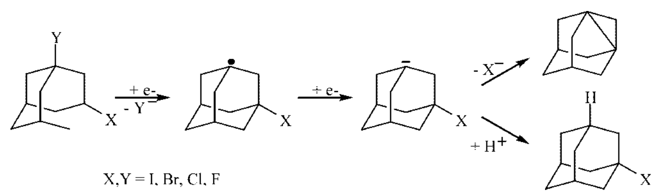



**Figure 7.** Morse curves for a concerted dissociative electron transfer at zero driving force.

**Scheme 21. Electrochemical Reduction Mechanism of 1,3-Dihaloadamantanes**




$$\Delta G^{\ddagger} = \Delta G^{\ddagger}_{0,\mathrm{ct}}\left(1 + \frac{\Delta G°}{4\Delta G^{\ddagger}_{0,\mathrm{ct}}}\right)^2 \quad (17)$$

$$\Delta G^{\ddagger}_{0,\mathrm{ct}} = \frac{\lambda_0 + \lambda_i + D_R}{4} \quad (18)$$

Since it involves a contribution of the bond dissociation energy of the cleaving bond, the intrinsic barrier associated with concerted dissociative (eq 18) ET processes is larger than that corresponding to outer-sphere ET reactions. The contribution of the reorganization of the solvent molecules is similar to that used in the Marcus−Hush model and can be determined from equations (7–9).

The DET model has been extensively studied and successfully tested.[185,542,554] Early *ab initio* calculations provided evidence for the validity of the Morse curve approximation.[555] Numerous subsequent studies have been concerned with exploring different aspects of the dissociative electron transfer theory and experimentally confirming various theoretical predictions under homogeneous and heterogeneous electron transfer conditions.[28,47,49,79,467,468,556–561]

Application of the DET gave good agreement for the experimental and predicted intrinsic barrier values for the electrochemical reduction of organic halides.[467,468] An interesting feature of Savéant's ET theory is that bond dissociative energies for ET cleaving bonds can be estimated from experimental data. Here again, electrochemistry was of tremendous assistance in obtaining C−halogen bond dissociation energies for substituted benzyl and anthracenyl halides,[558] vicinal dihalides[559] and different series of dihalo bicylic compounds.[560] A similar investigation for sulfonim salts undergoing a C−S bond cleavage on reduction[28] and for *N*-halosultams where a N−halogen bond is cleaved has been reported.[79] The application of the DET theory to a study of bicyclo dihalides not only made it possible to estimate the C−Cl, C−Br and C−I bond dissociation energies within the series but also provided the tools to rationalize the effect of the presence of the nearby halogen atoms. A typical example is provided in Scheme 21. The electrochemical reduction of 1,3-dihaloadamantanes yields ring closure products as well as monohalo derivatives resulting from expulsion of the best halide ion leaving group. The study showed that product selection takes place at the level of the carbanion produced by reduction of the one-electron reductive cleavage radical as a result of the competition between an intramolecular $S_N2$ reaction and protonation. It was found to depend on the nature of the second halogen. Thus the relative yield of the ring closure product varies from almost 1 to 0 as the second halogen goes from I to Br, to C1, and to F. These variations in the product distribution as well as in the reduction potentials of the series investigated were rationalized using the DET theory. They are related to variations in the bond dissociation energy of the first carbon−halogen bond to be cleaved which results from through-space interactions (in adamantanes and bicyclopentanes) and through-bond interactions (in bicyclooctanes) in the radical produced by one-electron reductive cleavage and, to a lesser extent, in the starting dihalide itself.

The quadratic aspect of the activation energy-driving force relationship for DET (eq 17) has been recently revisited. "Classical" concerted ET mechanisms are in fact associated with large intrinsic barriers due to the participation of the bond dissociation energy of the cleaved bond (eq 18). Subsequently, since it is inversely proportional to the intrinsic barrier, the curved region of the expected parabolic pattern may be difficult to detect unambiguously. ET studies of a series of alkyl halides using electrochemically generated aromatic radical anions as electron domors have demonstrated this.[251,562–564] The use of homogeneous catalysis in such cases has the disadvantage associated with uncertainties regarding the kinetics of the ET. This is because, besides the approximate character of the cross-exchange relationship, the rate constant may also differ from one donor to another. More recently, Maran, Wayner, Workentin and their coworkers effectively addressed this issue in a number of highly valuable manuscripts, where they investigated a series of peroxides using both homogeneous catalysis and direct electrochemical reduction.[47–49,51,280,281,565] Peroxides present the "advantage" of having weak O−O bonds, ranging between 25 and 30 kcal/mol, and thus low intrinsic barrier values, overcoming the complication associated with alkyl halides and hence are ideally suitable for these studies. A typical example is provided in Figure 8. It presents the variation of the logarithm of the ET homogeneous and heterogeneous (Scheme 22) rate constants with the driving force for pivaloyl peroxide in dimethylformamide.

More examples will be presented in section 5.

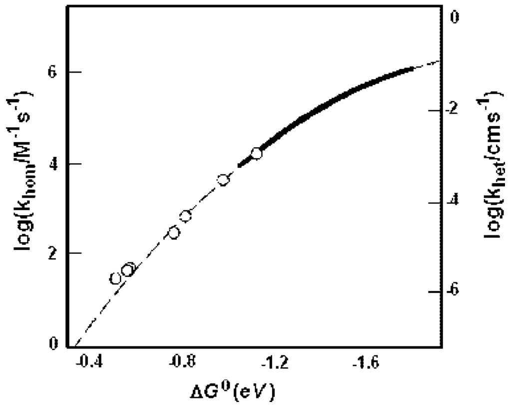
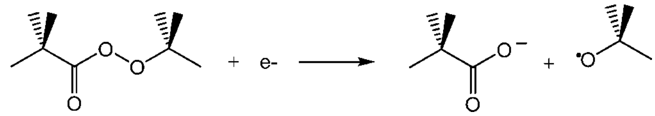



**Figure 8.** Comparison between (○) homogeneous ($k_{hom}$) and (−) heterogeneous ($k_{het}$) rate constants for the reduction of pivaloyl peroxide in DMF at 25 °C. The dashed line is the second-order fit to the data. Reprinted with permission from ref 281. Copyright 2001 American Chemical Society.

**Scheme 22. Electron Transfer to Pivaloyl Peroxide**



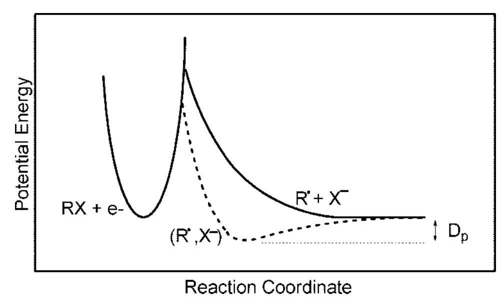




**Figure 9.** Morse curves for a "sticky" dissociative electron transfer at a zero driving force.

## 4.4. Sticky DET Model

Based on quantum chemical calculations charge−dipole (induced dipole) interactions between radicals and ions have long been shown to exist in the gas phase.[555,566–571] Many experimental results suggest, however, that despite their weakening in polar solvents such interactions may still survive and could therefore play a role in the dynamics of any chemical reactions where they are involved.[31,82,571–574] Since ET-initiated reactions are an excellent source of radicals and ions, the existence and effects of such interactions were both studied and modeled. Savéant successfully extended the DET theory to take into account the presence of such interactions between the fragments produced ("sticky" DET). This provides researchers with a tool not only to unravel the existence of in-cage interactions but also to quantify their extent, their strength, the factors controlling them and their impact on the ET reaction pathways.[31,82,571–574]

Quantum calculations showed that the existence of radical/ion interactions can be translated on the energy profile involving the dissociation of an ion radical intermediate in the gas phase through the appearance of an energy minimum at a distance where the interaction is at its maximum. They also showed that the energy profile curve can still be modeled using a Morse curve. Applying this in the framework of a reductive ET transfer to an initial molecule, one can view the effect of the involvement of in-cage interactions in a concerted ET mechanism as shown in Figure 9. This shows both the reactant and product potential energy curves for a DET involving the cleavage of a chemical bond.

The extension of DET to the case of radical-ion pair formation (eq 19) provided a new activation free energy−driving force quadratic relationship which involves the contribution of the interaction energy in the radical-ion pair ($D_P$).[571–577] The accuracy of this model has been demonstrated through its application to heterogeneous[571] as well as homogeneous[576,577] ET reactions.

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}_{0,\mathrm{sticky}}\left(1 + \frac{\Delta G^{o} - D_{\mathrm{P}}}{4\Delta G^{\ddagger}_{0,\mathrm{sticky}}}\right)^{2} \tag{19}$$

$$\Delta G^{\ddagger}_{0,\mathrm{sticky}} = \frac{\lambda_0 + (\sqrt{D_{\mathrm{R}}} - \sqrt{D_{\mathrm{P}}})^2}{4} \tag{20}$$

The existence of in-cage interactions affects the activation free energy through the introduction of a new work term ($D_P$). This involves the contribution of the interaction energy in the radical-ion pair, but also through an important decrease of the intrinsic barrier (eq 20) due to the replacement of $D_R$ by a smaller term ($[\sqrt{D_R} - \sqrt{D_P}]^2$) . This entails that a small interaction leads to an important decrease of the intrinsic barrier.

The intermediate formation of radical/ion pairs during the concerted reductive cleavage of carbon tetrachloride,[571,572] 4-cyanobenzyl chloride,[572]haloacetonitriles,[573] polychloroacetamides,[574] benzyl thiocyanates[31]and arene sulfenyl chlorides[82,83] has been reported. As expected, the strength of these interactions has been shown to depend on the Lewis acid−base properties of the fragments involved as well as on the nature of the solvent.[31,82,83,571–577] As a result of these interactions the concerted DET is accelerated and consequently leads to a decrease in the associated intrinsic barrier. The existence of such in-cage interactions during the electrochemical reduction of substituted benzyl thiocyanates[31] has been shown to affect the regioselective bond cleavage and hence the outcome of the reaction through the dissociation of a chemical bond that seems otherwise very stable. Some recent examples involving a sticky DET will be discussed in the following section.

## 4.5. Examples of Systems Undergoing a Sticky DET

### 4.5.1. Carbon Tetrachloride[571,572]

The electrochemical reduction of carbon tetrachloride in DMF provides a good example of a sticky DET mechanism. Although the reductive ET and bond breaking are concerted, the fragments generated interact in the solvent cage before diffusing apart. The presence of such interactions has been detected through analysis of the ET reaction kinetics and was rationalized using the "sticky DET theory". The first clues were obtained through the comparison of experimental and predicted data. The former were obtained through a linearization of the ET kinetic law of the CV potential window. The latter were obtained through application of the DET model, the activation free energy values and the transfer coefficient associated with the first ET step. The data clearly showed that the reaction is in reality faster than expected for a classical DET mechanism. Theoretical calculations clearly showed the presence of strong interactions in the gas phase and allowed their energies to be determined. Application of the "sticky" DET theory on the other hand lead to very good agreement between the predicted and the experimental data. The interaction energy $D_P$ that provided the best fitting is smaller than the corresponding calculated one because in-cage interactions are certainly weaker in a polar solvent such as DMF than in the gas phase.

Previous studies showed intriguing behavior for various reactants, and thanks to the development of this theory some of these can now be understood in terms of the involvement of in-cage interactions. The reduction of 4-cyanobenzyl chloride is a typical example in this context.

### 4.5.2. 4-Cyanobenzyl Chloride[572]

Another "sticky" DET mechanism that was observed is the electrochemical[572] and homogeneous reduction of 4-cyanobenzyl chloride.[576,578] Initial indications came from a comparison of the reduction potentials of the related benzyl bromide and 4-cyanobenzyl bromide. The difference was initially interpreted using the classical DET theory. It was attributed to a difference in the C−Br bond dissociation energy (BDE) caused by the introduction of the CN group.[552] This was later dismissed[572]in light of subsequent experimental[579,580] and theoretical[581] bond dissociation energy (BDE) data for the C−halogen bonds. Recent careful analysis indicates the involvement of clusters formed through in-cage interactions between the fragments generated in the concerted ET step.[572] As expected, a similar decrease in the intrinsic energy barrier leading to subsequent acceleration of the ET was observed. 4-Cyanobenzyl chloride and carbon tetrachloride have both been used to investigate the solvent effects on the nature of the cluster formation within the solvent cage.[572] These interactions have been shown to exist in polar solvents including formamide, ethanol, DMF and 1,2-dichloromethane. As expected the least polar solvent, 1,2-dichloromethane, was found to be the one showing the strongest interaction because the chloride anion is the least solvated. Interactions are intermediate in DMF because it is capable of solvating the chloride anion better than 1,2-dichloromethane but less than the other two solvents. The protic solvents formamide and ethanol showed the weakest interactions as expected since they are better able to solvate the chloride anions.

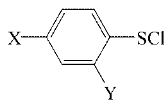
### 4.5.3. Haloacetonitriles[573]

The electrochemical reduction of haloacetonitriles provides another example of the involvement of in-cage radical/ion formation.[573] This study also investigated the influence of the nature of the leaving group on the extent of the interaction. Iodide showed the strongest interaction followed by bromide and then chloride. This provided more hints into the electrostatic nature of in-cage interactions. In addition to the electrochemical investigation that allowed determination of the kinetics and thermodynamics of the ET reaction, using quantum chemical calculations provided further support for the occurrence of a "sticky" DET mechanism. For all the compounds investigated, potential energy profiles as a function of the C−halogen bond exhibited a Morse curve shape with a clear minimum albeit at a distance larger than what would be expected for a radical anion. It was concluded therefore that the observed minima correspond to electrostatic radical/ion pairs. Here again, the variation of the C−halogen distances at the energy minimum, as a function of the leaving group, follows the same trends as the interaction energy. The observed C−halogen distances are 3.09, 3.23 and 3.45 for the chloro-, bromo- and iodoacetonitrile, respectively.[573] Another interesting result was the observed correlation between the interaction energy between the fragments in DMF and the radius of the halide anion. This also suggests that the interaction is electrostatic in nature.

### 4.5.4. Polychloroalkanes[470,574]

Other studies reported consisted of series of chlorinated compounds including aliphatic polychloroalkanes[470] and polychloroacetamides.[574] Electrochemical data, supported by ab initio calculations and application of the sticky DET transfer theory, allowed the determination of the interaction

**Chart 1**



X = $CH_3$, Y = H
X = H, Y = H
X = Cl, Y = H
X = $NO_2$, Y = H
X = H, Y = $NO_2$
X = $NO_2$, Y = $NO_2$

energies in the radical ion pairs generated. As a result of these interactions, a considerable decrease in the activation free energy of the reaction is observed for all compounds. Since the same chloride anion leaving group is expelled for this series after injection of an electron into the parent chlorinated molecule, the study provided an opportunity to unravel the effect of factors such as the dipole moment and the role of neighboring atoms within the radical moiety. This is in accordance with the assumption that the interaction within the radical/ion pair is electrostatic in nature. While data for the aliphatic polychloroalkane series provided evidence of the dependence of the interactions on the inductive effect generated by the susbtitutents on the radical moiety, the polychloroacetamide series, on the other hand, showed a decrease in the interaction energy as the number of chlorine atoms on the carbon involved in the dissociative process increases. A detailed analysis of the optimized reduced structures in the gas phase showed the importance of hydrogen bonding between the leaving chloride anion and the hydrogen of the amide group within the radical moiety in strengthening the cluster formation.

### *4.5.5. Sulfenyl Chlorides*[82,83]

Another example of cluster formation during a reductive dissociative cleavage is found in the electrochemical reduction of sulfenyl chlorides. The mechanism, its kinetics and thermodynamics were all analyzed, and their reduction was found to result in the cleavage of the S−Cl bond.[82,83] An initial investigation of the nitro-substituted structures showed that while a stepwise ET mechanism is observed during the reduction of 2-nitrophenyl sulfenyl chloride, a “sticky” DET mechanism involving the formation of a radical/anion (4-nitrophenyl sulfenyl/chloride) pair could not be ruled out for the 4-nitrophenyl sulfenyl chloride. This conclusion was based on intriguing observations that included an unexpectedly large difference between the reduction potentials of the two compounds. A subsequent study involved a more extended series of substituted benzyl sulfenyl chlorides (Chart 1). Not only was a change in the ET mechanism observed but, even more interestingly, a clear-cut example of a “sticky” DET mechanism was encountered. The factors controlling variations in the ET mechanism as well as the extent of the in-cage interactions between the reduction fragments were discussed on the basis of the DET theory as well as its extension to the case of in-cage interactions or “sticky” dissociative ET.[31,571−575] Theoretical calculations helped rationalize both the differences in the ET mechanisms and the cluster formation.

An intriguing initial observation was that the reduction potentials of 2-nitro- and 2,4-dinitrophenyl sulfenyl chlorides were more negative than those corresponding to other sulfenyl chlorides containing weaker electron-withdrawing or even electron-donating substituents. This is despite the presence of nitro groups. Although the investigation showed the presence of through-space S···O interactions in these two compounds, a consequence of the proximity of the ortho-nitro group to the sulfur atom,[82] this could only partially explain the intriguing order observed for the reduction potentials. A rigorous investigation of the electrochemical reduction reaction for this series revealed the involvement of strong in-cage interactions between the ET fragments produced thus leading to a “sticky” DET mechanism.

**Table 1. S−Cl Bond Dissociation Energy and Bond Length for 1a−f before and after Reduction**

| | 1a | 1b | 1c | 1d | 1e | 1f |
|---|---|---|---|---|---|---|
| $D_{S-Cl}$[a] | 40.13 | 40.45 | 39.97 | 47.65 | 53.29 | 53.83 |
| $d_{S-Cl}$ (**1**)[b] | 2.12 | 2.11 | 2.11 | 2.10 | 2.13 | 2.12 |
| $d_{S-Cl}$ (**1** + $e^-$)[b] | 2.86 | 2.85 | 2.83 | 2.79 | 2.45 | 2.42 |
| $\Delta d_{S-Cl}$[b] | 0.74 | 0.74 | 0.72 | 0.69 | 0.32 | 0.30 |

[a] Bond dissociation energy in kcal/mol. [b] Bond length in Å. Reprinted with permission from ref 83. 

The electrochemical investigation showed that the reduction of 2-nitro- and 2,4-dinitrophenyl sulfenyl chlorides follows a stepwise ET. Theoretical calculations supported this conclusion. Both the LUMOs of the neutral structures and the SOMOs, of the reduced forms, are more delocalized over the nitro-substituted aryl moiety. This indicates that the incoming electron is injected into the $\pi^*$ orbital thus yielding a radical anion intermediate. These reduced structures showed S−Cl distances shorter than those observed for the reduced forms of the other sulfenyl chlorides (Table 1). This is in accordance with the formation of “real” radical anions. Interestingly another minimum is obtained for a longer S−Cl distance for the reduced form for each of these compounds corresponding to the formation of radical−ion pairs and their dissociation as will be discussed in more detail later (section 6.1).

The other compounds within the series, including the 4-nitrophenyl sulfenyl chloride, showed a different behavior. The electrochemical data were not consistent with a stepwise mechanism, and the theoretical study showed that the LUMOs are located principally on the S−Cl group rather than the aryl moiety. Hence this increases the probability of injecting the extra electron directly into the $\sigma$ S−Cl bond and leads to its dissociation. A typical example is provided in Figure 10. This shows both the LUMO and the SOMO corresponding to the 4-nitrophenyl sulfenyl chloride and its reduced form, respectively. The SOMOs corresponding to the reduced forms clearly support this hypothesis as they are more localized on the S−Cl group. The reduced forms show S−Cl distances ranging between 2.79 and 2.86 Å. This indicates that these structures are not true radical anions but rather radical/ion pairs. This is in agreement with the electrochemical data, which indicates the implication of a concerted reduction process and not a stepwise one.

Consideration of the S−Cl bond distance as a result of the injection of an extra electron brought further insights. It showed that while the S−Cl bond distance increases by only 0.32 Å and no structural changes are observed for 2-nitro- and 2,4-dinitrophenyl sulfenyl chlorides after injecting an electron, the S−Cl bond distance increase is much larger for the other compounds (≥0.70 Å). 4-Nitrophenyl sulfenyl chloride is associated with an important rotation of the C−S bond on going from the nonplanar neutral molecule to its reduced form. This indicates that while the reduction of 2-nitro- and 2,4-dinitrophenyl sulfenyl chlorides leads to a radical anion through a stepwise ET mechanism (Scheme

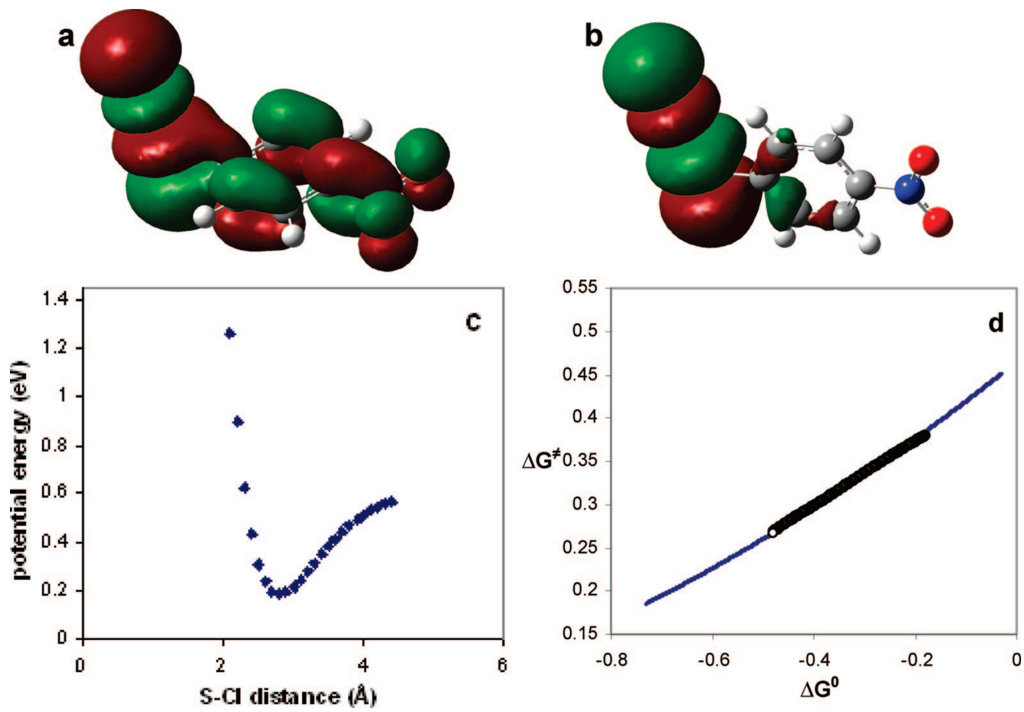



**Figure 10.** (a) LUMO for 4-nitrophenyl sulfenyl chloride and (b) SOMO of the reduced form. (c) Calculated (B3LYP/6-31G(p,d)) potential energy profiles in the gas phase for the 4-$NO_2PhS^{\bullet}/Cl^-$ pair. The plotted potential energy values correspond to the difference between the absolute values and a value lower than the minimum energy. (d) Experimental and predicted activation free energy vs standard free energy plots for 4-nitrophenyl sulfenyl chloride. (—) Predicted using the "sticky" DET model. (○) Experimental through convolution analysis. Adapted with permission from ref 83. Copyright 2006 American Chemical Society.

**Scheme 23. Reduction Mechanism for 2-Nitro and 2,4-Dinitrophenyl Sulfenyl Chlorides**

$$ArSCl + e^- \rightleftharpoons ArSCl^{\bullet -}$$
$$ArSCl^{\bullet -} \longrightarrow ArS^{\bullet} + Cl^-$$
$$2ArS^{\bullet} \longrightarrow ArSSAr$$
$$ArS^{\bullet} + e^- \longrightarrow ArS^-$$
$$ArS^{\bullet} + ArSCl^{\bullet -} \rightleftharpoons ArS^- + ArSCl$$
$$ArS^- + ArSCl \longrightarrow ArSSAr + Cl^-$$

23), for other compounds within the series this leads rather to a radical/anion pair through a "sticky" DET mechanism. This is in agreement with the electrochemical results. Gas phase potential energy profiles of the reduced forms along the cleaved S−Cl bond were calculated. The curves obtained are Morse curves and show a clear energy minimum along the cleaved bond indicating that, at least in the gas phase, strong interactions (0.277−0.383 eV) exist indeed between the fragments generated (radical/anion). A typical example is provided in Figure 10c for the 4-nitrophenyl sulfenyl chloride. An interesting result is that, for all these compounds (excluding the 2-nitro and 2,4-dinitro derivatives), the minimum energies are observed at large distances (2.8−2.9 Å) suggesting the formation of radical/anion pairs rather than real radical anion intermediates. These distances are also in very good agreement with the ones determined from the optimizations (Figure 10a,b (LUMOs)). It is worth noting that 4-nitrophenyl sulfenyl chloride shows a relatively higher interaction energy and that maximum interaction is observed at a slightly shorter distance compared to the other compounds (X = 4-$CH_3$, H, 4-Cl). This is in good agreement with the predictions that strong electron-withdrawing groups reinforce fragment clustering, as has been previously demonstrated.[571]

**Table 2. S−Cl Interaction Energy and Bond Length at the Minima**

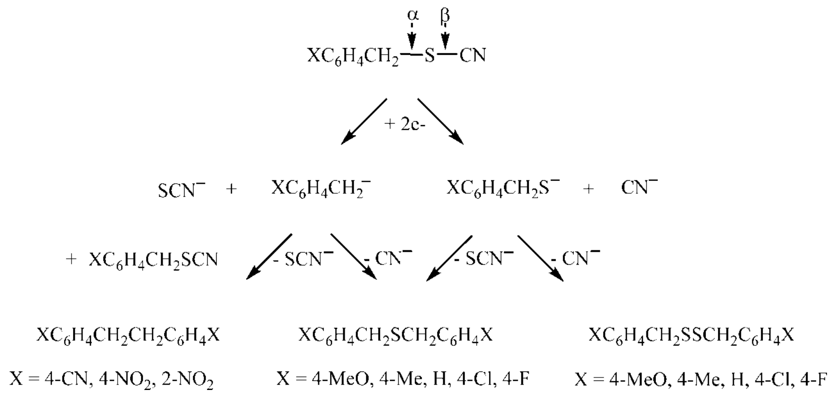
| X | 4-$CH_3$ | H | 4-Cl | 4-$NO_2$ |
|---|---|---|---|---|
| $D_P{}^a$ (eV) | 0.277 | 0.283 | 0.285 | 0.383 |
| $D_P{}^b$ (eV) | 0.020 | 0.020 | 0.020 | 0.150 |
| $d_{S-Cl}$ (**1**)$^c$ | 2.9 | 2.9 | 2.9 | 2.8 |

$^a$ Interaction energy calculated in gas phase. $^b$ Interaction energy used for "sticky" DET model. $^c$ Bond length at the minima in Å. Reprinted with permission from ref 83. Copyright 2006 American Chemical Society.

This series (X = 4-$CH_3$, H, 4-Cl, 4-$NO_2$) was further investigated using both the "classical" (eq 17) and the "sticky" DET models (eq 19). A comparison of the intrinsic barriers as a function of the driving force obtained through either model with the experimental data from a convolution analysis of the cyclic voltammetric data was carried out.[83]

Figure 10d shows both the experimental and the predicted (using eq 19) activation free energy as a function of the driving force for the reduction of 4-nitrophenyl sulfenyl chloride. The experimental data are in accordance with that obtained using the "sticky" DET model (eq 19) rather than the "classical" DET (eq 17). A similar behavior is observed for the other 3 sulfenyl chlorides (X = 4-$CH_3$, H, 4-Cl). For all compounds the predicted activation energy is larger than the experimental one. To obtain the best fit, the interaction energy $D_P$ has been adjusted and a very good fit is obtained for values of $D_P$ lower than the ones estimated through gas phase calculations (Table 2). This is expected since these interactions are smaller in solution due to the solvation of the fragments. It is worth noting that for 4-nitrophenyl sulfenyl chloride, with a strong electron-withdrawing group, a stronger interaction compared to the others (X = 4-$CH_3$, H, 4-Cl) is seen in solution as well.[571] These data confirm the existence of radical/anion pair formation during the electrochemical reduction of 4-substituted phenyl sulfenyl

**Scheme 24. Products of the Electrochemical Reduction of Substituted Benzyl Thiocyanates**




chlorides (X = 4-$CH_3$, H, 4-Cl, 4-$NO_2$). The application of DET to these compounds thus follows a concerted mechanism, which leads to the formation of a radical/anion cluster. As shown here and in full agreement with what has been reported in previous work,[571–574] in-cage interactions such as these in solution, even when moderate compared to the gas phase, strongly affect the dynamics of the process involved. In this case this is translated into an important decrease in the activation free energy of the electrochemical reduction.

Another consequence of such in-cage interactions is the extent of the difference between the standard reduction potentials with the reduction peak potentials for such compounds. The difference between these two parameters (631 mV for X = 4-$CH_3$; 558 mV for X = H; 552 mV for X = 4-Cl, and 148 mV for X = 4-$NO_2$) is lower than that usually seen for "classical" concerted ET processes (more than 700 mV). In the particular case of 4-nitrophenyl sulfenyl chloride, which shows the strongest interaction between the 4-nitrophenyl thiyl radical and the chloride anion, this difference is the smallest. This demonstrates that this compound is reduced near its standard reduction potential unlike what would have been observed without the involvement of such strong interactions.

### *4.5.6. Benzylthiocyanates*[31]

These present another excellent example of a "sticky" DET mechanism. More importantly, it is the first example where the formation of a radical/ion cluster during the reduction of a series of such compounds not only speeds up the reaction but completely changes its outcome thanks to the presence of a competing reaction. The electrochemical reduction of ring-substituted benzyl thiocyanates in fact showed the potential formation of 3 major compounds resulting from the dissociation of one of two chemical bonds within the structure: $CH_2$−SCN bond (α-cleavage) or $CH_2$S-CN bond (*β*-cleavage) (Scheme 24). The disulfide can result only from a *β*-cleavage, the dibenzyl derivative only from an α-cleavage and the mono-sulfide can arise from either.

Based on the electrochemical data, a stepwise electron transfer mechanism derivatives was readily assigned to the nitro-substituted derivatives. These undergo only an α-cleavage on reduction leading to the substituted dibenzyl derivatives (Scheme 24). For all other compounds including the cyanobenzyl thiocyanate, based on the electrochemical investigation the stepwise mechanism was ruled out. Theoretical calculations of the LUMOs provided further support for this conclusion (see further details in section 6.1).[31] Using an extension of the DET transfer model to the case of radical ion formation/dissociation (section 6.1), a comparison of the dynamics of the two cleavages led to the conclusion that if a radical anion intermediate is formed during the reduction of the benzyl thiocyanates, as is the case for the nitro-substituted derivatives, then α-cleavage would be favored from both a thermodynamic and a kinetic point of view (see section 6.1).[31]

While based on these considerations the difference in the ET mechanism could readily be understood, it is somewhat more difficult to rationalize the regioselective bond cleavage for the benzyl thiocyanates series using the "classical" DET theory. It could be hypothesized that the introduction of an electron-withdrawing group into 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 in fact not the case, and the theoretical data reported clearly shows that the nature of the substituent has very 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.

In the "classical" DET theory, the thermodynamics of a dissociative ET to a substrate RX can be described by eq 3. In the case of the non-nitro-substituted benzyl thiocyanate series (X = 4-MeO, 4-Me, H, 4-Cl, 4-F, 4-CN), the thermodynamics would be in favor of an α-cleavage. This is mainly due to the large difference in the BDE between the α and *β* bonds and despite the very positive value of $E^\circ_{CN^\bullet/CN^-}$ compared to $E^\circ_{NCS^\bullet/NCS^-}$[31] (a situation which favors a *β*-cleavage) as discussed in section 6.1.[31] This shows that from a thermodynamic point of view, assuming there is no interaction between the fragments produced, the α-cleavage should be favorable in all cases. Using eq 18 to consider the kinetics for such a concerted ET mechanism, the α-cleavage would again be favored mainly due to 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 therefore that using the "classical" DET theory, which is successfully applicable to concerted processes not involving the intermediate formation of radical/ion pairs (through radical-induced dipole interactions), an α-cleavage would be favorable from both a thermodynamic and a kinetic point of view for the benzyl thiocyanate series. Since the electrochemical results show that for the series of substituted benzyl thiocyanates following a concerted ET mechanism (X = 4-MeO, 4-Me, H, 4-Cl, 4-F, 4-CN) only the 4-cyanobenzyl chloride undergoes an exclusive α-cleav-

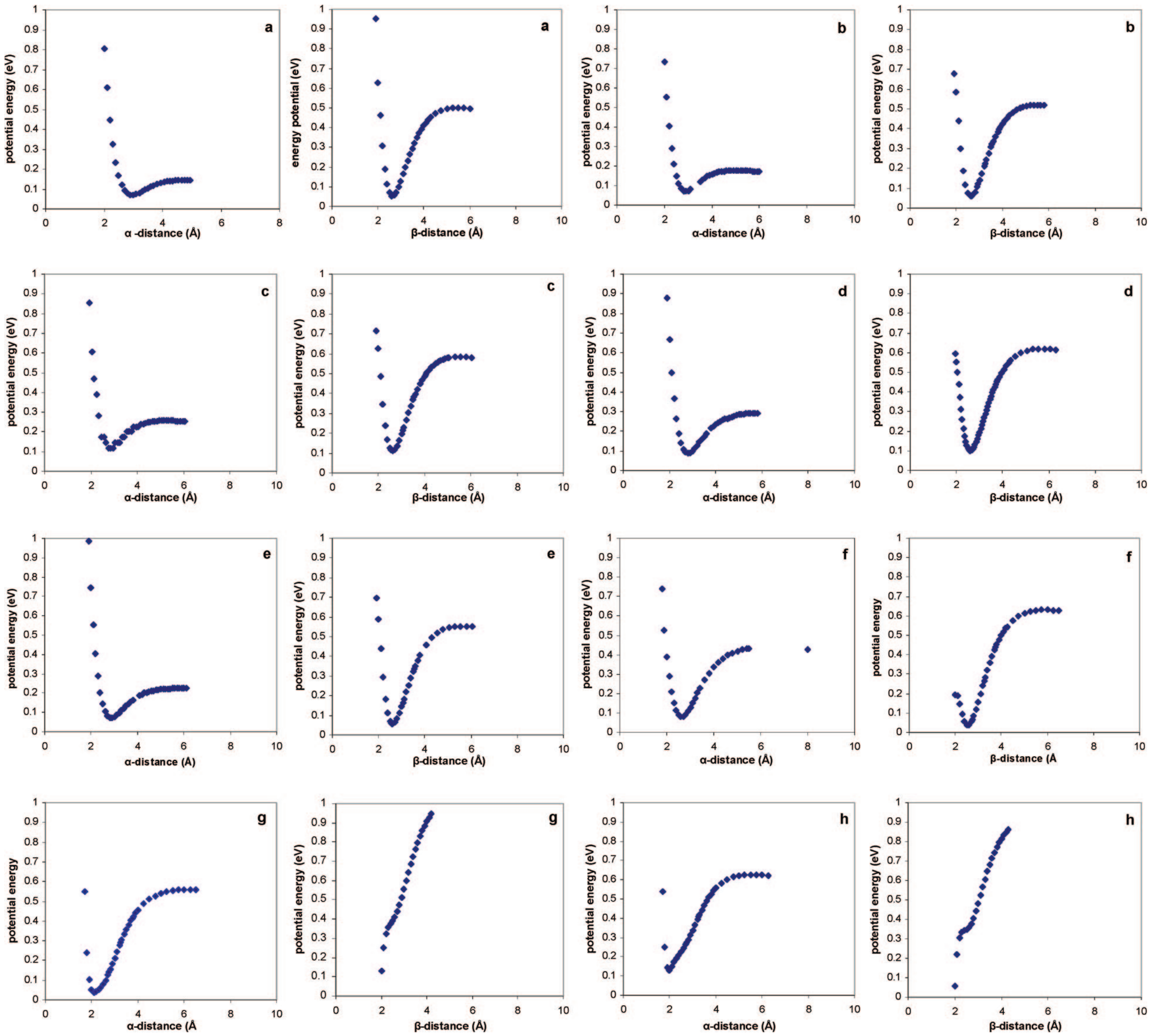



**Figure 11.** Calculated (B3LYP/6-31G(p,d)) potential energy profiles in the gas phase for the XBn•/SCN⁻ pair (left) and XBnS•/CN⁻ pair (right) for (a) X = 4-MeO; (b) X = 4-Me; (c) X = H; (d) X = 4-Cl; (e) X = 4-F; (f) X = 4-CN; (g) X = 4-$NO_2$ and (h) X = 2-$NO_2$. What is represented in panels a−h is not the absolute potential energy but rather the difference between the absolute value and a value lower than the minimum energy. Adapted with permission from ref 31. Copyright 2006 American Chemical Society.

age on electrochemical reduction it was necessary then to understand the reason behind the observed regioselectivity.

This intriguing behavior suggested the potential presence of strong in-cage interactions between the β-cleavage fragments produced.[571–574] The potential involvement of radical/anion pairs, and their effect on the observed regioselective bond cleavage during the electrochemical reduction process of this benzyl thiocyanate series, has been investigated. The "sticky" DET model and energy profile calculations for both cleavage modes for the series were used.

Figure 11 shows the gas phase potential energy profile for the reduced forms 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.

For compounds undergoing a concerted ET (X = 4-MeO, 4-Me, H, 4-Cl, 4-F, 4-CN), the Morse curves obtained showed 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). Bond length values at the minimum energy ($a_\alpha$ and $a_\beta$) as

**Table 3. Interaction Energies and Minimum Energy Bond Lengths**

| $XC_6H_4CH_2SCN$ | $a_\alpha{}^a$ (Å) | $a_\beta{}^b$ (Å) | $D_{P(\alpha)}{}^c$ | $D_{P(\beta)}{}^d$ | $\Delta D_P$ (eV) |
|---|---|---|---|---|---|
| X = 4-MeO | 3 | 2.6 | 0.073 | 0.447 | 0.374 |
| X = 4-Me | 2.9 | 2.6 | 0.106 | 0.459 | 0.353 |
| X = H | 2.9 | 2.6 | 0.137 | 0.471 | 0.334 |
| X = 4-Cl | 2.8 | 2.6 | 0.202 | 0.618 | 0.416 |
| X = 4-F | 2.9 | 2.6 | 0.154 | 0.495 | 0.341 |
| X = 4-CN | 2.6 | 2.5 | 0.351 | 0.589 | 0.238 |
| X = 4-$NO_2$ | 2.1 | | | | |
| X = 2-$NO_2$ | 2.0 | | | | |

[a] Distance at minimum potential energy along α-bond. [b] Distance at minimum potential energy along β-bond. [c] Interaction energy ($E_{final} - E_{minimum}$) for the bond α (in eV). [d] Interaction energy ($E_{final} - E_{minimum}$) for the bond β (in eV). Reprinted with permission from ref 31. Copyright 2006 American Chemical Society.

well as the interaction energies are reported in Table 3. These data show real trends. It is clear that for all compounds, except the cyano-substituted one, the interaction energies between the β-cleavage produced fragments are significantly higher than those for the α-cleavage ones. In addition, minimum energies are also observed at lower bond length values for the $\beta$-cleavage compared to the α-cleavage. An interesting result is the fact that 4-cyanobenzyl thiocyanate, which has been shown to follow an ET mechanism similar to the other compounds in the series, undergoes exclusive reductive cleavage of the α-bond. A smaller difference ($\Delta D_P$) between the interaction energies of the α and $\beta$ cleavage fragments ($D_{P(\alpha)}$ and $D_{P(\beta)}$) is observed compared to others in the series. For 4-cyanobenzyl thiocyanate, which has a stronger electron withdrawing group, both $D_{P(\alpha)}$ and $D_{P(\beta)}$ are higher. This is in agreement with predictions.[571] However, the relative increase of $D_{P(\alpha)}$ is more substantial. For all the benzyl thiocyanates investigated and in both energy profile curves (along the α and $\beta$ bonds), the minimum energies are observed at large distances (2.5 to 3 Å). This suggests that the formation of radical/anion pairs rather than real radical anion intermediates is involved. The minimum energy bond distance $a_\alpha$ is substantially larger than $a_\beta$. This is in agreement with the observed differences in the interaction energies $D_P$. It is worth nothing that not only are both $a_\alpha$ and $a_\beta$ smaller for the cyano derivative than for the other compounds in the series but the relative decrease in $a_\alpha$ is larger than that of $a_\beta$. This is a clear indication that, at least in the gas phase, the interaction between the α-cleavage fragments for this compound ($NCBn^\bullet$, $SCN^-$) is stronger than for the others.

Analysis of the nitro-substituted benzyl thiocyanates (Figures 11g,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 α bond distances ($a_\alpha$) than those seen for other compounds within the series (Table 3). This indicates the formation of real radical anions 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. This involved the intermediate formation of a radical anion as a result of the injection of an electron into the parent nitro-substituted molecules with subsequent exclusive formation of products resulting from the α-cleavage.

The calculations show, therefore, that for the benzyl thiocyanates undergoing a concerted electron transfer mechanism (X = 4-MeO, 4-Me, H, 4-Cl, 4-F), the interaction between the $\beta$-cleavage-produced fragments is more important than those observed for the α-cleavage. This interaction would counterbalance the advantage of the α-cleavage which is mainly due to the weak bond dissociation energy of the α-bond compared to the $\beta$. As a result, these two processes (α and $\beta$ cleavage) should be closer from a thermodynamic point of view than initially thought without the consideration of in-cage interactions. These calculations also show that for 4-cyanobenzyl thiocyanate the interactions are similar in both cases and that the main factor is still the BDE, which is in favor of the α-cleavage. For the nitro-substituted derivatives, the calculations are in complete agreement with the electrochemical data as well as earlier results which proposed a stepwise ET mechanism. A quantitative analysis was not possible because the calculations were done in the gas phase and do not take into consideration the solvent effects. Qualitatively, however, these calculations showed real trends implying that the existence of strong in-cage interactions through a sticky DET mechanism intermediate is a plausible explanation of the observed regioselective bond cleavage encountered within this series.

Further work is required which might provide additional experimental examples involving the intermediate formation of such radical-ion pairs ($\sigma$-radical ions). These would provide more insights into the factors controlling such phenomenon as well as into their consequences on chemical reactions.

## 4.6. "Almost" Dissociative Electron Transfer

An interesting case is that encountered in the reductive DET to series of organic sulfides and disulfides. The overall reduction mechanism is well established. In an overall two electron process it leads either to two thiolate anions, through the dissociation of the disulfide S−S bond, or to a thiolate and a carbanion, through the dissociation of the sulfide C−S bond.

The mechanism through which the first electron transfer takes place, on the other hand, initially viewed as a "classical" stepwise mechanism, has been the subject of many investigations. Only recently has more light been shed on the "unique" features accompanying this process. In particular the relatively high intrinsic barrier associated with ET to organic sulfides[23–26] and disulfides[60,61,64–66]compared to other compounds undergoing a stepwise DET such as aromatic halides that are well described by the outer-sphere electron transfer model was discussed. The uniqueness of some sulfides and disulfides is that they are believed to involve the intermediate formation of a $\sigma$ radical anion on accepting the extra electron rather than a $\pi$ radical anion, as is the case for aromatic halides. In an early study using pulse radiolysis experiments in water for the reduction of a series of disulfides by hydrated electrons, it was suggested that the electron was injected into the S−S bond, yielding an unstable radical anion. The subsequent dissociation rate was found to depend on the environment surrounding the S−S group.[62] The existence, stability and characteristics of such S-centered intermediates have been the subject of numerous studies.[582–585]

Building on earlier work, more recent studies involving both homogeneous ET using electrochemically generated radical anions and heterogeneous electrochemical reduction at glassy carbon and mercury electrodes led to unraveling the details of the initial ET. It was suggested that while some of these compounds follow a "classical" stepwise ET mechanism, where a $\pi^*$ radical anion is formed as a discrete intermediate as a result of the initial electron uptake, other compounds within these series involve the intermediate formation of a $\sigma^*$ radical anion. Besides the experimental data, theoretical quantum calculations were used to further investigate the nature of the electron hosting orbital, the initially-generated intermediate as well as the factors controlling them.[64,584]

An important feature to emerge from these and earlier studies was the slow electron transfer rate under both homogeneous and heterogeneous conditions, pointing to a relatively large intrinsic barrier not in accordance with that usually found for stepwise electron transfer mechanisms. Here the intrinsic barrier is the sum of the solvent and inner contributions (eqs 4, 5). In outer-sphere ET reactions the inner reorganization energy is usually very small[474,586] and can even be neglected in most cases. This is because the reduced (or oxidized) molecule undergoes very little internal changes as is the case when a $\pi^*$ radical anion is formed upon injection of an electron into a hosting $\pi^*$ orbital. In this case, the solvent is the main contributor and the ensuing intrinsic barrier is small. Recent studies showed that the relatively large intrinsic barrier values for some sulfides and disulfides are due to the important inner reorganization of these compounds on going from neutral structures to the corresponding $\sigma^*$ radical anion. The electron is injected into the $\sigma^*$ orbital of either the disulfide S−S or the sulfide C−S bond. Quantum chemical calculations showed that the main reorganization consists of an important increase in the length of the chemical bond undergoing cleavage (C−S or S−S). The resulting transient species is a loose radical anion. The electron has been added to a more localized and rigid $\sigma^*$ orbital to generate a two center three-electron bond accompanied by important structural perturbation. The formation of these types of intermediates with important structural changes implies that they should be associated with large intrinsic barriers. Such studies confirm that in this case the contribution of the inner reorganization to the intrinsic barrier cannot be neglected but that it is even more important than that corresponding to the solvent reorganization. This inner reorganization has been found to be around 70 to 80% of the total intrinsic barrier.

In the investigation of series of symmetrical[61,65,66]and unsymmetrical[64] aromatic disulfides, the nature of the intermediate has been shown to strongly depend on the nature of the substituent on the aryl group. With electron donating or weakly attracting substituents, both the LUMO in the neutral species and the SOMO of the reduced form are very localized. The ET rate is very slow because of its association with a high intrinsic barrier. With electron withdrawing substituents, the LUMO orbital has some $\pi$ character and the SOMO is relatively more delocalized hence decreasing the inner reorganization energy associated with the ET. For 4,4′-dinitrodiphenyl disulfide, a $\pi$ radical anion is formed first. The reaction is fast and the reorganization energy very small, and the mechanism can be described by the outer-sphere ET model.

In another study, the reduction of diphenyl 4-methoxyphenyl sulfide in DMF, using glassy carbon and mercury,[26] also suggested the involvement of an intermediate $\sigma$ radical anion. Through the injection of an electron into the $\sigma^*$ orbital important structural perturbations were induced in line with the behavior of previously mentioned sulfides.[24,66]

As discussed above, the characteristics of a system undergoing a sticky DET mechanism are very similar to those undergoing an almost dissociative ET mechanism. In both cases the intrinsic barrier is higher than for a stepwise mechanism but still lower than that for a concerted mechanism.

A very recent and relevant study by Tanko and co-workers for the reduction of 1,2-diacetylcyclopropane using a combination of electrochemistry, homogeneous catalysis and theoretical calculations is somewhat intriguing.[22] The homogeneous catalysis showed that the ET is the rate limiting step. The transfer coefficient obtained from cyclic voltammetric data and convolution analysis indicated a similar conclusion but showed, however, that the α value is only slightly lower than 0.5, i.e., larger than that usually found for concerted dissociative electron processes. Theoretical calculations at the UHF/6-31G* level did not show the existence of a radical anion intermediate generated directly through injection of one electron into the 1,2-diacetylcyclopropane, and only a structure corresponding to the ring-open distonic radical anion was obtained. Convolution analysis allowed the determination of the experimental log $k_{het}$-driving force plot, which was compared to those obtained using DET, sticky DET and stepwise (Marcus-type) ET models. These involve considerable internal reorganization and loose radical anions. While the experimental plot has been found to differ from that determined from the DET model, it was possible to fit both the plot obtained using the sticky dissociative model, through introduction of an interaction energy ($D_P$) between the fragments generated (eq 19), and that using the Marcus relationship which introduces a larger internal reorganization energy. The authors suggested, however, that neither of these two mechanisms is in fact plausible. On the one hand the interaction energy used to allow fitting between the experimental and the sticky dissociative model data is too large (0.98 eV) and even larger than the one calculated for interaction in the gas phase (0.42 eV). On the other hand, theoretical calculations ruled out the existence of a stable radical anion structure with a close cyclopropyl ring for 1,2-diacetylcyclopropane. The authors suggested that in this reduction the extra electron is more likely injected in a concerted manner, but into a delocalized structure where the bond length between the two carbon atoms bearing the acetyl groups is stretched. This induces a considerable lowering of the LUMO orbital energy.

An interesting aspect of the study of 1,2-diacetylcyclopropane is that it clearly showed that by applying both models and including appropriate parameters (increased internal reorganization or introduction of the in-cage interaction), the same outcome was obtained as expected.

## 5. Experimental Implications of Electron Transfer Theories

Electron transfer models have been extensively tested, and their validity has been well documented. Their application can provide valuable kinetic and thermodynamic information if the nature of the ET mechanism is ascertained. This might not always be obvious as for example is the case when the ET is the rate limiting step. Here the distinction between a concerted process and a stepwise one with a very fast dissociation of the single ET product can be challenging. Unraveling the correct ET mechanism may therefore require the initial determination of a series of important parameters related to the reaction, and sometimes a comparison between experimentally determined parameters and the predicted ones using these theoretical models is required. Kinetic and thermodynamic parameters such as the standard redox potential, the activation energy (or rate constant), the driving force and the transfer coefficient are all relevant. Variation of the activation energy, the rate constant, and the transfer coefficient with the driving force can all be of tremendous assistance.

### 5.1. Stepwise/Concerted Electron Transfer Mechanisms

Because the kinetics and thermodynamics of an ET are intrinsically related to its mechanism, unraveling the nature of the mechanism is an ongoing issue that attracts great attention. Besides its fundamental importance, ascertaining the ET mechanism is necessary for a better understanding of the overall reaction mechanism. It also maximizes exploitation of the intermediates involved in synthetic strategies. The most accurate way to ascertain a stepwise ET mechanism is the experimental detection of the single electron intermediate. Techniques such as cyclic voltammetry, homogeneous catalysis, spectroelectrochemistry and laser flash photolysis can all be efficiently used to that end. Even when experimentally unconfirmed, intermediate formation and its subsequent rapid reaction cannot be completely ruled out. In electrochemistry, cyclic voltammetry (CV) can be efficiently used through analysis of peak characteristics to obtain accurate mechanistic, kinetic and thermodynamic data. An interesting parameter that can provide, under these conditions, information regarding the ET mechanism is the transfer coefficient $\alpha$. Ambiguous situations may, however, be encountered, and a more profound analysis is needed as will be discussed in the following section.

### 5.1.1. Transfer Coefficient

When the single ET product cannot be detected experimentally (high scan rate[239,253] and homogeneous catalysis[181,239,253]), the transfer coefficient ($\alpha$), which is directly related to the intrinsic barrier (eq 21), can be used to probe the mechanistic nature of the first ET in dissociative processes. The transfer coefficient is a description of how the activation energy varies with the driving force (eq 21).

$$\alpha = \frac{\partial \Delta G^{\ddagger}}{\partial \Delta G^{\circ}} = \frac{1}{2}\left(1 + \frac{\Delta G^{\circ}}{4\Delta G_0^{\ddagger}}\right) \tag{21}$$

Equation 21 ensures two important aspects. One concerns the expected $\alpha$ values for the two mechanisms. Because the driving force for concerted processes is negative enough to compensate for the high intrinsic barrier which includes the bond dissociation energy of the cleaved bond, the transfer coefficient is expected to show a value significantly lower than 0.5. For the stepwise mechanism, where an ion radical is an intermediate, the driving force is much smaller. This leads to a transfer coefficient value that is close to or higher than 0.5. This has been intensively investigated especially for heterogeneous ET reactions at electrodes since the driving force can easily be controlled over a wide range by varying the potential, and also because the transfer coefficient can more readily be determined either from the peak width (eq 22) or from the variation of the peak potential with the scan rate in CV (eq 23).[282,396,468,555,558,560] Nevertheless, examples of homogeneous ET reactions are available.

$$\alpha = \frac{RT}{F}\left(\frac{E_P - E_{P/2}}{1.85}\right) \tag{22}$$

$$\alpha = -29.5\left(\frac{\partial E_P}{\partial \log v}\right)^{-1} \tag{23}$$

The use of convolution analysis has been particularly important when investigating the variation of the transfer coefficient as a function of the driving force. Indeed apparent values of transfer coefficient ($\alpha_{app}$) can be obtained from the ln $k_{het}$ vs $E$ data by using eq 24.

$$\alpha_{app} = -\frac{RT}{F}\frac{\partial \ln k_{het}}{\partial E} \tag{24}$$

$\alpha_{app}$ is related to $\alpha$ through the double-layer correction by the following equation:

$$\alpha = \alpha_{app}/(1 - \partial \varphi^{\#}/\partial E) \tag{25}$$

where $\varphi^{\#}(E)$ is the difference between the potential of the bulk solution and the potential at which the substrate is located when the electron transfer takes place. It depends on the nature of the working electrode. It has been shown that, even when these properties are unknown, uncorrected transfer coefficient values provide a reasonable representation of the process. This is because these values do not differ much from the true ones. For a mercury electrode, where the double-layer correction is better defined, $\alpha_{app}$ has been shown to be smaller than $\alpha$ by only 3%.[278,280] Differentiation is accomplished by linear regression of the experimental data within small potential segments (~20 mV).

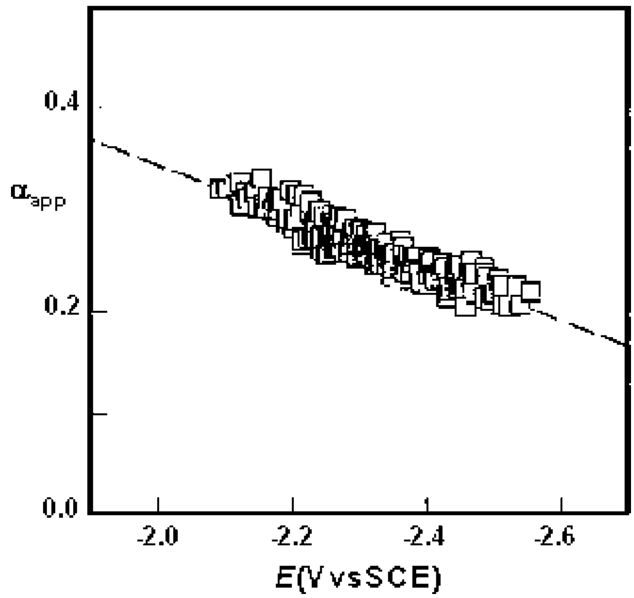
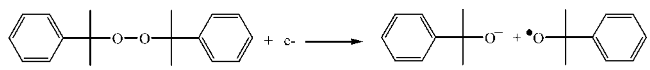



**Figure 12.** Potential dependence of the apparent transfer coefficient ($\alpha_{app}$) for the reduction of dicumyl peroxide in DMF/0.1 M TBAP at the Hg electrode at $T$ = 25 °C. Adapted with permission from ref 48. Copyright 1997 American Chemical Society.

**Scheme 25. Dissociative Electron Transfer to Dicumyl Peroxide**



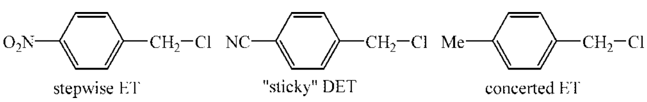
The second important aspect of eq 21 is that it implies that, for all reported ET mechanisms, assuming only one mechanism is taking place, a linear relationship is expected for the transfer coefficient with the driving force. This aspect was initially explored by Savéant and Tessier, who demonstrated the linear relationship between the transfer coefficient and the driving force for a series of organic compounds in aprotic solvents taking advantage of the well-defined double layer at the mercury electrode.[567] Later on, using analysis of the electrochemical reduction of a series of dialkyl peroxides through the use of convolution analysis, a convincing investigation of the linearity of the transfer coefficient–driving force plot was achieved. A typical example is provided in Figure 12, showing the plot of the electrochemical reduction of dicumyl peroxide (Scheme 25).[48]

Examples where a nonlinear variation is observed have also been reported. This is an indication that the electron transfer reaction is not ruled by a single mechanism and will be discussed in section 5.5.

## 5.2. Factors Controlling the Dissociative Electron Transfer Mechanism

Factors controlling the ET mechanism have been extensively studied to such a degree that it is possible to predict, in many cases, the ET mechanism for a specific substrate. Factors affecting the ET in a dissociative ET mechanism can

**Chart 2**




be divided into two main categories: internal and external factors. The internal factors are intrinsic to the investigated species and are related to its molecular structure, whereas the external factors are related to the ET reaction conditions. These include the initiation mode and the solvent as well as the driving force and the factors affecting it such as the temperature.

### 5.2.1. Internal Factors

Molecular structure is the most important factor contributing to the type of ET mechanism occurring. The different parameters related to the substrate molecular structure which can affect the ET mechanism include the LUMO or HOMO orbitals, the bond dissociation energy (BDE) of the cleaved bond and the nature of the leaving group. The LUMO or HOMO orbitals depend on whether the ET is reduction or oxidation.

One approach to understanding these structure-related parameters is by considering a potential radical ion intermediate formed by ET to a substrate RX and the factors affecting both its stability and the dynamics of its decomposition. If we consider a reduction, the driving force for the dissociation of the radical anion can be written as follows (eq 26):

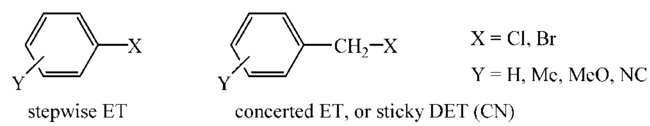
$$\Delta G_0 = E^0_{RX/RX\bullet-} - E^0_{RX/R\bullet+X-} = E^0_{RX/RX\bullet-} + D_{R-X} - E^0_{X\bullet/X-} - T\Delta S_{RX/R\bullet+X\bullet} \quad (26)$$

This equation represents the difference in the reaction free energy between the two possible ET mechanisms. It suggests that three main factors need to be considered when analyzing the dichotomy between the mechanisms: the standard reduction potential of the reactant ($E°_{RX/RX\bullet-}$), the BDE of the cleaved bond ($D_{R-X}$) and the standard oxidation potential of the leaving group ($E°_{X\bullet/X-}$). The weaker the bond, the more positive $E°_{X\bullet/X-}$ is, the more negative $E°_{RX/RX\bullet-}$ is and hence the more favorable the thermodynamics of the concerted mechanism. In most cases, more than one factor can differ changing from one structure to another. Structures can, however, be designed either to affect only one of these factors or at least to minimize changes in the others. The result is that individual factors can be studied separately. Many such studies have been conducted and the effects of the main factors well rationalized.[181,185,469,542]

The effect of the standard reduction potential can readily be understood in terms of the reductive ET mechanism in the following series of substituted benzyl halides (Chart 2):

The nitro group lowers the $\pi^*$ orbital energy to such a degree that it becomes the hosting orbital of the incoming electron leading to a radical anion intermediate via a stepwise ET mechanism.[558] The methoxy group increases the energy of the orbital to the point that the electron is directly injected into the $CH_2-Cl$ $\sigma^*$ orbital causing its simultaneous cleavage in a concerted manner. For the cyano group, which is less electron withdrawing than the nitro group and hence exerts an intermediate effect, the mechanism is concerted but involves the formation of a radical/anion cluster through in-cage interactions.[572]

**Chart 3**




**Scheme 26**

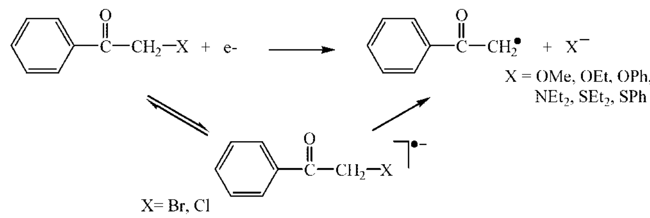



Chart 3 shows a few examples where the main factor in determining the ET mechanism is the BDE. The incoming electron is injected in all cases into a similar orbital, and the dissociation of the cleaving chemical bond yields the same leaving group. The observed differences in the ET mechanisms are mainly due to the difference in the BDE values. With the weaker benzyl−halide[558] chemical bond the mechanism for the aryl halides is concerted involving the intermediate formation of a radical anion, through a stepwise ET mechanism.[588]

The nature of the leaving group can also be the controlling factor in determining the mechanism of the initial ET even if this is most often associated with a change in the BDE of the cleaved bond. Examples have, however, been encountered where the nature of the leaving group (hard vs soft) has been shown to be the predominant factor affecting the ET mechanism (Scheme 26).[73]

Many other examples have been reported where the molecular structure has been shown to have a major impact on the ET mechanism within the same series of compounds: the electrochemical reduction of sulfonium salts[28] and more recently a series of chloroorganic compounds.[470]

For additional examples regarding the role of molecular structure in defining the ET mechanisms, the reader may refer to the extensive literature available[181,469,542] which includes an excellent recent book by Savéant.[185]

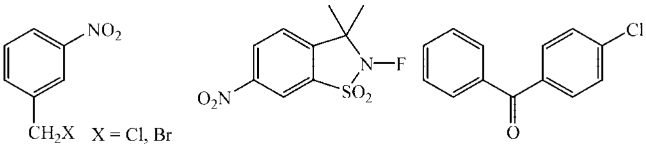
### 5.2.2. External Factors

External factors include the driving force for the reaction, which may depend on the ET initiation mode, or may even be controlled within the same initiation mode. Another factor is the solvent used since it can affect the stability of the intermediate involved, which is usually a radical or an ion, and hence influences the rate of the reaction.

**Solvent.** The main role of the solvent in ET reactions[72,80] is through stabilization or destabilization of the intermediates involved although sometimes reactants and products are affected too.[589−593] It has been long recognized that, for stepwise ET reactions, increasing the solvent polarity, or ion pairing, increases the associated reorganization energy.[266,553]

The electrochemical reduction of α-substituted acetophenones provided an interesting example in this context. This study showed that these compounds follow a stepwise mechanism and the solvent reorganization energy associated with this step is the main component of the total reorganization energy since the internal contribution was found to be small. The intrinsic barrier associated with ET is relatively large and does not depend much on the nature of the substituent.[72]

Chart 4



Another interesting study was of the decomposition rate constants of a series of radical anions formed from 3-nitrobenzyl chloride and bromide, *N*-fluoro-7-nitro-saccharin-sultam and 4-chlorobenzophenone (Chart 4) in acetonitrile. The addition of increasing amounts of water to the electrolytic solutions induced a decrease in the decomposition rate constants associated with an apparent ease of reduction of the parent molecules.[80] Indeed earlier pulse radiolysis studies in water had provided much smaller decomposition rate constants for 3-nitrobenzyl chloride and bromide.[594]

Although the stabilization/destabilization effects of the solvent on the intermediates in these processes were extensively investigated,[72,80,266,553,589–593] a more recent study clearly showed that the nature of the solvent might in specific cases favor one ET mechanism over another.[595] Electron transfer to para and ortho nitro-substituted benzyl chlorides and bromides in DMF[80,558,596] and water[594,597] also pointed to a stepwise mechanism in all cases. It was shown that the corresponding radical anions dissociate faster in DMF. It is worth mentioning that different initiation modes have been used in these investigations including electrochemical,[558,596] photochemical,[596] and pulse radiolysis,[594,597] implying that the driving force of the reaction is not necessarily the same from one initiation mode to another. Quantum chemical calculations showed, however, that despite the difference in the driving force, the solvent does indeed affect the stability of these radical anion intermediates.[595] A more stable $\pi$ radical anion has been found when the potential energy profiles of the radical anions taking the solvation into consideration were compared to those in the gas phase. Figure 13 shows the calculated energy profiles for 3-nitrobenzyl chloride where the first minimum, corresponding to the $\pi$ radical anion, is clearly more distinct in the presence of solvent molecules.

Cyano substrates provided similar insights into the solvent's role.[595] The potential energy profiles calculated for 4-cyanobenzyl chloride are shown in Figure 14. In the gas phase, the energy showed only one minimum at a large C−Cl distance corresponding to a $\sigma$-radical anion and a very small inflection at a shorter C−Cl distance. The latter is where the $\pi$-radical anion is expected and becomes only slightly more distinct after introducing the solvent. Experimentally, however,[595] whereas 3- and 4-cyanobenzyl chlorides and bromides were found to follow a concerted mechanism in DMF under electrochemical as well as photochemical initiations,[558,596] instead the pulse radiolysis reduction in water[594,597] showed the intermediate formation of the corresponding radical anions through a stepwise mechanism. The acceleration of the radical anion decomposition for the cyano compounds, compared to the nitro ones, can be understood in terms of the thermodynamic stability of the radical anions (eq 26) as discussed previously. The cyano group is a weaker electron withdrawing substituent than the nitro group, and therefore the standard reduction potential corresponding to the parent structure is more negative. Because of the large driving force window offered by the electrochemical and pulse radiolysis initiation modes (reducing power ranging from −1.7 to −3 V vs SCE),[595] the difference in the ET mechanism has been attributed to the solvent effects. Consequently, even if these calculations provided a qualitative insight into the role of the solvent in affecting radical anion stability, this effect is most likely underestimated.

**Driving Force.** Not only does the driving force associated with an ET reaction have an important impact on the resulting mechanism; it can also affect the following steps. The analysis of the effect of the driving force can be undertaken either using the same initiation mode or by studying the redox characteristics of a reactant under different initiation modes. These cases will be discussed in the following sections (5.3 and 5.4).

## 5.3. Controlling the Driving Force through Changing the Initiation Mode

The ET initiation mode can strongly affect the driving force associated with ET reactions and may in specific cases even induce different ET mechanisms. This was first encountered for two specific sulfonium salts: 4-cyanobenzylmethylphenyl sulfonium salt and phenyldimethyl sulfonium salt.[540,596,598] The first follows a stepwise mechanism under electrochemical reduction and a borderline mechanism under photochemically-induced reduction. The second follows a borderline mechanism under electrochemical reduction and a concerted mechanism under photochemically-induced reduction. This behavior may be understood on the basis of the driving force on changing the initiation mode from electrochemistry to photochemistry.

Another case where both ET mechanisms are observed for different initiation modes has been shown for a series of cyanobenzyl halides. With 4-cyanobenzyl chloride,[596] 3-cyano- and 4-cyanobenzyl bromides[558] a concerted ET mechanism is followed under electrochemical reduction in DMF. Using pulse radiolysis in water, however, showed that the three compounds now follow a stepwise ET mechanism.[599] As discussed in the previous section, it has been shown that the mechanistic transition in this case can be explained by the important role of the solvent rather than the change in the driving force when the initiation mode is changed. 4-Cyanobenzyl chloride showed a concerted ET mechanism under photochemically-induced reduction in DMF despite a large increase ($\geq 1$ eV) in the driving force,[596] compared to the electrochemical reduction. It is worth noting that previous photochemical studies of benzyl and 4-cyanobenzyl bromides[600–603] suggested a stepwise ET mechanism based on quantum yield determinations. Assigning the ET mechanism in photoinduced ET reactions, based on quantum yield, has been shown to be problematic as will be discussed in the following.

## 5.4. Photochemically-Initiated Dissociative Electron Transfer

The photochemical initiation of ET reactions is a well-known process, and the dynamics for a large range of reactants has been investigated from both experimental and theoretical standpoints.[102,604–606] Dissociative ET reactions are among the processes investigated[102,606] because they have been used to overcome back ET in an effort to limit the wasted energy.[606–608] The kinetics of both the forward and back ET rate constants as well as of those of the associated bond fragmentation in both donors and acceptors have all

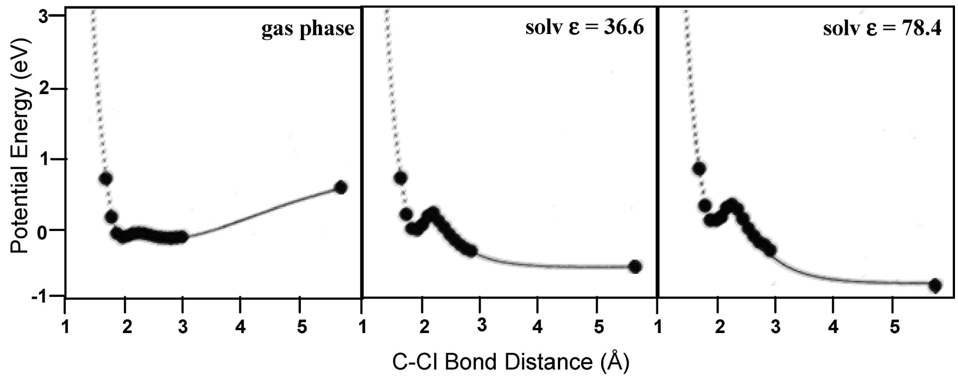



**Figure 13.** Potential energy profiles as a function of the C−Cl distance for 3-nitrobenzyl chloride. Adapted with permission from ref 595. Copyright 2004 American Chemical Society.

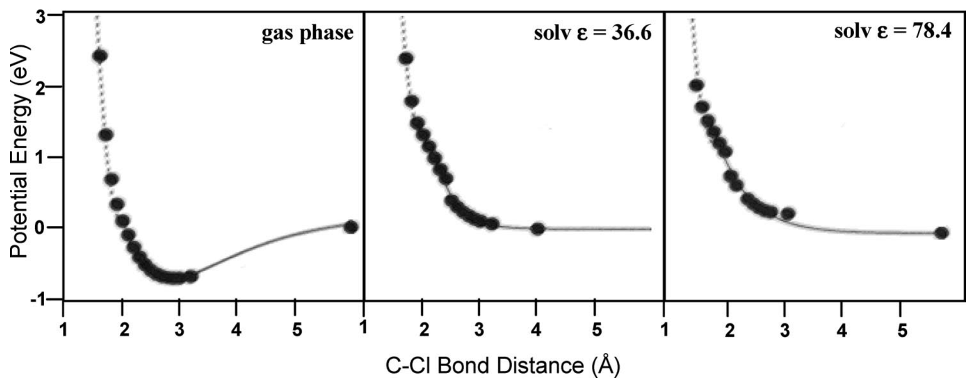
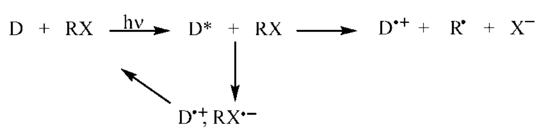



**Figure 14.** Potential energy profiles as a function of the C−Cl distance for 4-cyanobenzyl chloride. Adapted with permission from ref 595. Copyright 2004 American Chemical Society.

**Scheme 27. Bond Cleavage and Back Electron Transfer in Photoinduced Electron Transfer Reactions**




been investigated.[102,603,606,608–623] The mechanistic assignment of ET mechanisms has attracted particular attention. When the single ET direct product formed through a stepwise process is not detected, distinction between the two mechanisms becomes more complicated and has been based mainly on quantum yield determination.[600–603]

It has therefore been suggested that, whenever back ET and fragmentation are the only processes consuming the ET-generated product (Scheme 27), a concerted process should provide a quantum yield close to 1 due to the fact that back ET is eliminated. Consequently, a quantum yield lower than 1 would indicate a stepwise ET associated with the formation of a single ET product and still involving back ET. One example which, according to this hypothesis, was concluded as following a stepwise mechanism is the photoassisted reduction of carbon tetrachloride using a series of electron donors.[624,625] The reaction using pinacols as electron donors was found to be particularly inefficient, and quantum yields substantially lower than 1 were obtained for the photoassisted ET process.[624,625] These results were interpreted as suggesting the existence of a carbon tetrachloride radical anion intermediate.[624,625] Other examples include the photochemical reduction of benzyl and 4-cyanobenzyl bromides using diphenylmethyl radical[600] and pinacols[624] as sensitizers. Another interesting example, where the ET mechanism was assigned based on quantum yield determination, is the photoassisted ET to a series of sulfonium salts.[598] The quantum yields corresponding to the photochemical reduction of 4-cyanobenzylmethylphenyl sulfonium tetrafluoroborate, using a series of electron donor sensitizers including 9-phenylanthracene, 2-ethyl-9,10-dimethoxyanthracene and perylene, were significantly lower than 1 (0.65−0.77).

Recent advanced electrochemical investigations of the reduction of both carbon tetrachloride[571,572] and 4-cyanobenzylmethylphenyl sulfonium salt[540,596] showed, however, that both compounds are reduced following a concerted process where the ET and the bond cleavage are simultaneous. 4-Cyanobenzylmethylphenyl sulfonium salt follows a concerted ET on electrochemical reduction.[28] Under photochemically-initiated reduction using 2-ethyl-9,10-dimethoxyanthracene as a sensitizer, the same compound showed competition between a concerted and a stepwise ET mechanism.[596]

For carbon tetrachloride, significant interaction has been shown to exist between the chloride anion and the trichloromethyl radical generated through the concerted ET.[571,572] One might intuitively argue that the difference in behavior observed for these compounds under different initiation modes may be understood on the basis of the difference in the driving forces for each mode. While this has been shown to be indeed the case for specific systems, theoretical and experimental studies by Savéant's group[540,596,626] provided important insights and questioned the validity of such mechanistic assignments based on quantum yield values. These studies demonstrated that a quantum yield might indeed be significantly lower than 1 despite the occurrence of a concerted ET mechanism. The studies showed that the quantum yield for a concerted system would be 1 only if the ET at the ground state is nonadiabatic, that is, if there is no electronic coupling in the transition state. Figure 15, which

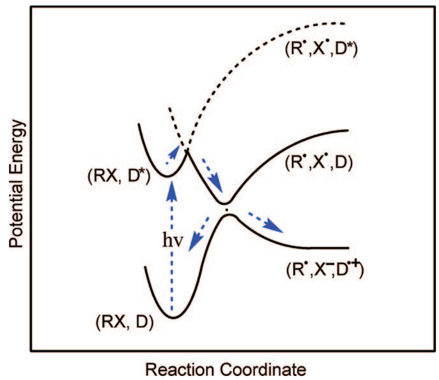



**Figure 15.** Section of the zero-order (•••) and first-order (—) potential energy surfaces along the reaction coordinate in cases where stretching of the cleaving bond is the dominant factor of nuclei reorganization. Adapted with permission from ref 540. Copyright 2000 American Chemical Society.

shows the potential energy profiles for the reactant and product ground states as well as the reactant excited state, along the cleaving bond distance as the main coordinate, makes it possible to conceptualize this. Under photoassisted conditions, the ET between the excited state of the donor and the substrate would be expected to exclusively yield the products only if the electronic coupling in the transition state of the ground ET is inexistent. Otherwise, the back electron process will take place giving the initial reactant and a quantum yield lower than 1 despite the concerted nature of this reaction. Determination of the quantum yield as a function of the electronic matrix coupling element, $H$, was achieved using a semiclassical treatment[429,515–517,534] of a simplified model (Figure 15) based on Savéant's theory of DET.[467–469,627,628] Even in a case where the back ET is disfavored, this treatment lead to a simplified equation between the quantum yield and $P$ (eq 27). This is the probability of the system to remain on the upper first-order curve, and where the quantum yield is not necessarily 1:

$$\Phi = \frac{1}{1+P} \tag{27}$$

Applying the Landau–Zener model,[429,515–517,534] the probability $P$ is related to $H$ through eq 28:

$$P = 1 - \exp(-\pi^{3/2}H^2/h\nu_{\mathrm{eff}}\sqrt{RTD}) \tag{28}$$

where $\nu_{\mathrm{eff}}$ is the effective frequency at which the system crosses the intersection region and $D$ is the dissociation energy of the fragmenting bond.

Consideration of the solvent reorganization, which is an important parameter in DET reactions, provides a similar partition of the system starting from the photoinduced reaction transition state, and leading to either the caged products (dissociative ET) or caged ground state reactants (back ET). The probability of the system to remain on the upper first-order curve has a similar expression with the exception that now the reorganization energy ($\lambda_0$) is included (eq 29):

$$P = 1 - \exp[-\pi^{3/2}H^2/h\nu_{\mathrm{eff}}\sqrt{RT(D+\lambda_0)}] \tag{29}$$

Further evidence that a stepwise photoinduced ET process can show a quantum yield close or equal to one is available.[626] Two expressions have been obtained for the quantum yield depending on the nature of the back ET. When the back ET takes place in the normal region, the quantum yield

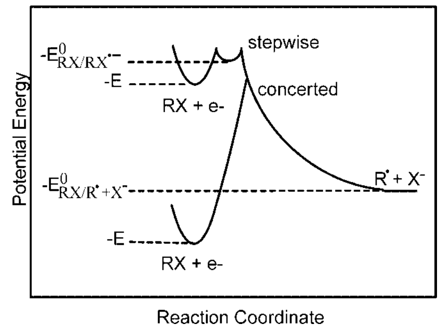



**Figure 16.** Electron transfer mechanism dependence on driving force.

is related to the probability $P$ through an equation similar to the concerted ET case (eq 27). $P$ can also be expressed through an equation similar to the concerted ET one where $D$ is replaced by the expression $([\sqrt{D_{RX}} - \sqrt{D_{RX^{\bullet -}}}]^2)$ . This term involves the bond dissociation energies of the cleaving bond in the initial substrate, $D_{\mathrm{RX}}$, and the reduced form, $D_{\mathrm{RX}^{\bullet -}}$ (eq 29). Under these conditions as in the previous case, it is very unlikely that the quantum yield will reach 1. When the back ET takes place in the inverted region, a different expression is obtained (eq 30). In addition to the rate constant for the back ET in the caged fragment cluster ($k_{-\mathrm{act}}$), the quantum yield, Φ, is a function of the rate constant of the fragment separation ($k_{\mathrm{sp}}$) and the cleavage of the reduction product intermediate ($k_{\mathrm{c}}$).

$$\Phi = \frac{k_{\mathrm{sp}} + k_{\mathrm{c}}}{k_{\mathrm{sp}} + k_{\mathrm{c}} + k_{-\mathrm{act}}} \tag{30}$$

## 5.5. Mechanism Transition within the Same Initiation Mode

As a result of variation of the driving force, borderline situations where both stepwise and concerted ET mechanisms coexist, or transition from one to another is observed, have been encountered for some compounds. Changes in the driving force for a given ET reaction can readily be achieved by varying either the electrode potential in electrochemistry or the electron donor in homogeneous thermal and photochemical initiations.

This behavior demonstrates that the nature of the ET process is dictated by the energetic advantage of one pathway over another rather than by the existence of the single ET product (intermediate). Figure 16 shows how the ET mechanism of a chemical process can change from concerted to stepwise by changing the driving force. This transition is accompanied by a change in the activation free energy of the reaction (the activation free energy involving the contribution of the cleaved bond in addition to the solvent reorganization energy). The standard potential also changes. Careful analysis of the ET reaction dynamics can in fact provide insights into the existence of such a transition.

Since the driving force can easily be controlled through variation of the electrode potential, most available examples have been studied using electrochemistry. Mechanism transitions have, nevertheless, been reported for homogeneous thermal and photochemical ET reactions.[576,596] Analysis of the transfer coefficient variations with either the scan rate[28,629] or the potential[282] is the main avenue for studying such a mechanistic transition.

As discussed in section 5.1, eq 21 predicts a linear variation for the transfer coefficient α with the driving force.

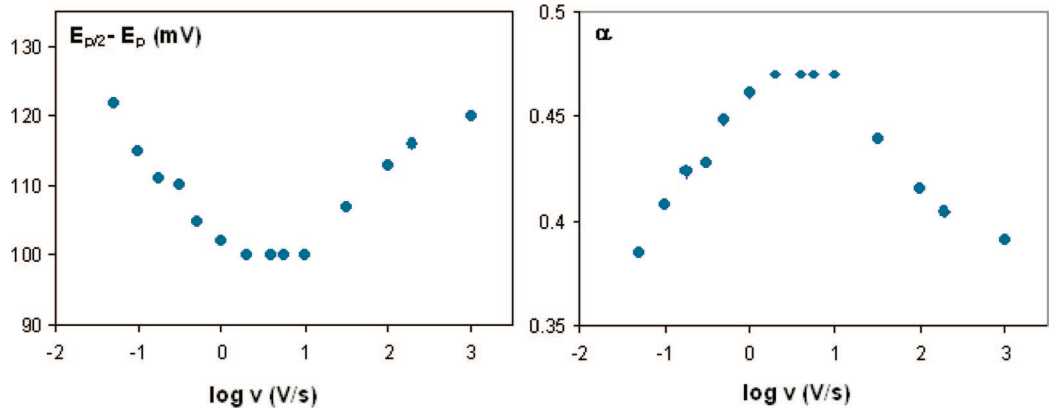
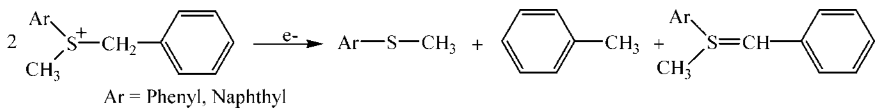



**Figure 17.** Variation of the peak potential and the transfer coefficient with the log($v$) for benzylmethylphenyl sulfonium salt. Adapted with permission from ref 28. Copyright 1994 American Chemical Society.

**Scheme 28**




However, only a few experimental systems have shown a nonlinear variation indicating a transition between concerted and stepwise mechanisms as a function of the driving force. In addition to conventional voltammetric analysis, the convolution approach is a powerful tool for studying the intricate details of such electrode processes.

### *5.5.1. Triphenylmethyl Phenyl Sulfide*

An early example pointing to a transition from a stepwise to a concerted ET mechanism is the reduction of triphenylmethyl phenyl sulfide using homogenous catalysis.[23] Under these conditions (section 3.1) one can progressively change the driving force of an ET reaction by choosing a series of donors (in the case of a reductive process) with gradually increasing (or decreasing) standard potentials. Electron transfer to triphenyl phenyl sulfide was studied using a series of stable electrochemically-generated radical anions allowing a variation of the driving force over a range of almost 0.6 eV. Estimation of the rate constants of the homogeneous ET and investigation of the variation of the activation energy as a function of the driving force led the authors to conclude that a stepwise/concerted mechanism transition takes place as the driving force is increased. It was reported in the same study[23] that the reduction of benzyl phenyl sulfide and diphenylmethyl phenyl sulfide, structurally related to triphenylmethyl phenyl sulfide, led to the formation of a radical anion intermediate through a stepwise ET mechanism.

### *5.5.2. 4-Nitrocumyl Chloride*

Another example of such a mechanistic transition in homogeneous ET reactions is found in the reduction of 4-nitrocumyl chloride using a series of electron donors.[578] The use of 2-nitropropanate, as the electron donor, leads to a concerted DET where the ET and the C−Cl bond fragmentation are simultaneous. On the other hand other donors (duroquinone and 1-nitro-4-(1,1,2-trimethyl-2-nitropropyl)-benzene radical anions) induce a stepwise ET reductive process.

### *5.5.3. Sulfonium Salts*

In electrochemistry, a clear-cut example of a transition in the ET mechanism is encountered in the electrochemical reduction of a series of sulfonium salts.[28] Analysis of the variation of the peak width ($E_p - E_{p/2}$) and the transfer coefficient α (Figure 17), with the scan rate in CV, showed a nonlinear variation for two compounds in the series (Scheme 28). After ruling out the involvement of any adsorption of the ylide produced, through addition of an acid during the electrochemical study, this nonlinear dependence of the peak width and α with the driving force provided an indication of a transition between a concerted and a stepwise mechanism for these two compounds.

### *5.5.4. Iodobenzenes*

The electrochemical reduction of iodobenzene and 4-methyliodobenzene showed similar behavior: the transfer coefficient first increased with increasing scan rates before decreasing as the scan rate continued to increase.[629] To further support the idea of a transition between the concerted and stepwise mechanism for these compounds, electrochemical data were collected at two different temperatures, namely, 298 and 329 K. Since the transfer coefficient is a function of the intrinsic energy barrier, which is directly related to temperature, it can be expected that, for a compound showing such borderline ET mechanism behavior, a change in the temperature may allow experimental detection of the transition, as was the case here. It is well established that in general aromatic halides follow a stepwise ET reduction mechanism.[283,469,588,628] Their behavior can be understood based on the previous discussion regarding the dependence of the ET on the structure. Compared to substituted phenyl chlorides and bromides,[588] the C−halogen bond in iodides is weak enough to induce a mechanism transition. Their $\pi^*$ orbital is less accessible than that of other aromatic iodides such as naphthalene iodide,[630] which follow a stepwise mechanism.

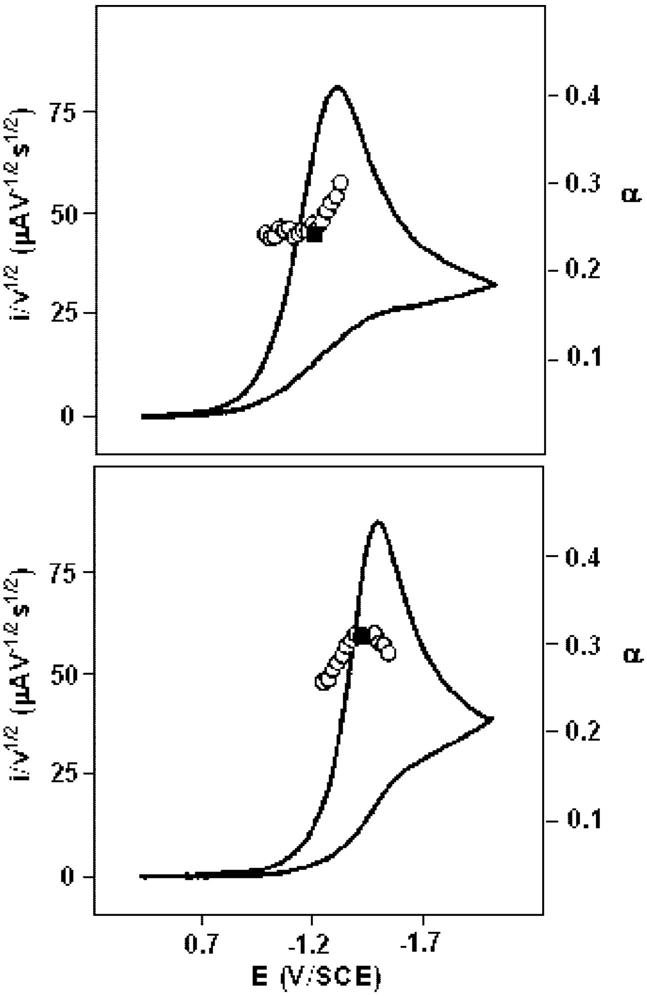



**Figure 18.** Background-subtracted cyclic voltammograms for the reduction of *tert*-butyl 4-cyanoperbenzoate (1.47 mM), at 0.2 V/s (top) and 20 V/s (bottom), in DMF/0.1 M TBAP at a glassy carbon electrode, $T = 25$ °C. Also reported in the graphs are the convolution α data (○) and the peak-width α datum (■). Reprinted with permission from ref 278. Copyright 1997 American Chemical Society.

### *5.5.5. Peroxides*

The electrochemical reduction in DMF of a series of of ring-substituted perbenzoates was studied using CV. Combined with convolution analysis this provided insight into the occurrence of both ET mechanisms for a range of driving force values.[278,279,281] One advantage of convolution analysis is that it provides the transfer coefficient as a function of the electrode potential within a single cyclic voltammogram. This together with the fact that CV makes it easy to change the driving force allowed a clear demonstration of the transition between the two mechanisms. This is shown in Figure 18. At the lower scan rate, the transfer coefficient is initially constant and increases gradually as the electrode potential approaches the peak potential. At the higher scan rate, as the electrode potential is scanned along the reduction peak, the transfer coefficient first increases then decreases.

### *5.5.6. Arylthiocyanates*[30]

The heterogeneous ET kinetics of the dissociative electrochemical reduction of 4-methylphenyl thiocyanate and 4-methoxyphenyl thiocyanate have also been explored using a combination of CV and convolution analysis.[48,51,278–281] In addition to its heterogeneous reduction at the electrode, the starting material is consumed by a chemical reaction (nucleophilic attack) in solution through a special autocatalysis process (Scheme 13). Hence it was necessary to perform the experiments at low concentrations and high scan rates to suppress this homogeneous process (reaction 3, Scheme 13).

The resulting $\alpha_{app}$ vs $E$ plots for these compounds shown in Figure 19 definitively show that the electrode process is not ruled by a simple ET mechanism. The wavelike dependence of α is very similar to those previously reported when a transition between the concerted and stepwise ET mechanisms is present.[28,629] For 4-methylphenyl thiocyanate scan rates ranging from 7.2 to 80 V/s were used. The $\alpha_{app}$ vs $E$ plots are characterized by a maximum at ca. −2.14 V, corresponding to an average α value of 0.31. The same maximum was obtained within only 20 mV at any scan rate thus providing α data in the appropriate range (Figure 19a).

A similar behavior is seen for 4-methoxyphenyl thiocyanate (Figure 19b) which shows a maximum at ca. −2.08 V, corresponding to an average α value of 0.33. Such nonlinear behavior clearly reflects a change of the electrode mechanism as a function of the potential. It is worth noting that, in the specific case of aryl thiocyanates, this mechanistic transition has an important impact on the overall mechanism since it favors the occurrence of the autocatalytic process at low scan rates and eliminates it at higher scan rates. At low scan rates, the electrochemical reduction of the aryl thiocyanate yields the arylthiyl radical at the electrode, through a concerted process (reaction 1′, Scheme 13). This radical is immediately reduced yielding the arenethiolate (reaction 2, Scheme 13).

## *6. Intramolecular Dissociative Electron Transfer*

Intramolecluar ET between a donor and an acceptor within the same structure has been widely investigated. Most studies in this context were concerned with long-range nondissociative ET processes in macromolecules. This is largely attributed to the importance of ET reactions in natural and biological processes as well as to their potential use in a wide range of applications mainly in the fields of sensors and electronic devices.[631–636] Examples include electron transfer in DNA,[637–641] originally motivated by the biological relevance of such routes to oxidative and other DNA damage.[642–645]

Nondissociative intramolecular ET has been extensively reviewed,[493–502,646–648] hence this chapter will focus on dissociative processes. In intramolecular DET reactions, attention has focused on the dissociation of radical ions where a chemical bond is broken yielding a radical and an ion. In most cases the intramolecular ET takes place between close centers within the radical ion structure. Increasingly, however, interest is turning toward the investigation of long-range intramolecular dissociative ET where the two centers are separated by a molecular spacer (or bridge).[102,281,506,649–660] It is predicted that the dynamics of intramolecular dissociative ET reactions, like nondissociative ones, will depend on factors such as the nature of the donor, acceptor, molecular bridge (spacer) and the distance separating them. The available data for ET through molecular bridges in nondissociative processes provides a sound base for further investigation. It is worth noting that the side reactions that initially appear as a complication can in fact provide additional information through the monitoring of specific

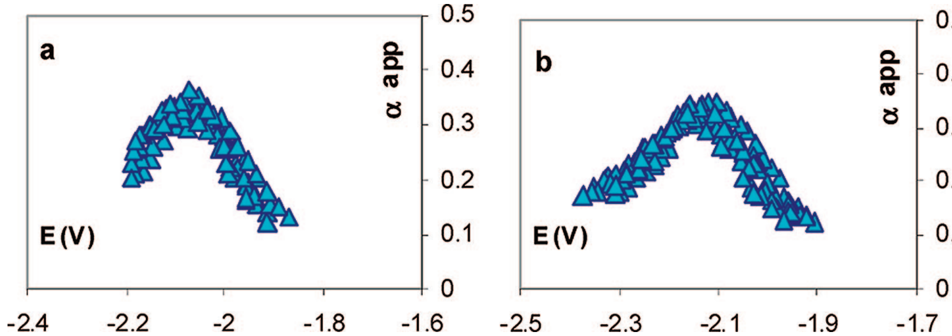
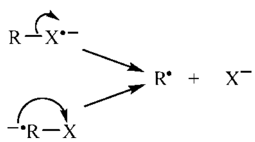



**Figure 19.** Variation of $\alpha_{app}$ with $E$ for (a) **1** (0.85 mM) and (b) **2** (0.69 mM) at scan rate $v = 7.2$, 10, 20, 30, 40, 60 and 80 V/s. Reprinted with permission from ref 30. Copyright 2003 American Chemical Society.

**Scheme 29. Homolytic and Heterolytic Modes for the Dissociation of a Radical Anion**




intermediates as a result of careful design of the structures investigated.

In this section the progress made in understanding dissociative intramolecular ET will be discussed.

## 6.1. Association/Dissociation of Radicals and Ions

Due to the importance of radicals and radical ions as intermediates in many chemical and biochemical processes the dynamics of their dissociation has been intensively studied. An example is that of aromatic radical ions which have been shown to be fundamental intermediates in the formation of Grignard reagents[661–665] as well as in DNA damage.[666–671] Using a wide range of techniques the dissociation of radical ions has been investigated both theoretically and experimentally.

The dissociation of radical anions has been more thoroughly investigated than the reverse reaction which consists of the combination of a radical and a nucleophile. One important reaction in which both the formation and the dissociation of radical anions are involved is the $S_{RN}1$ reaction (Scheme 2), which is of interest from both a synthetic and a fundamental point of view.[76,84,266,282,284,672–681]

The important progress made in understanding transfer mechanisms and the factors controlling them provided the tools to better tailor the subsequent chemical steps. This is particularly true for the fragmentation of radicals (or radical anions) generated as the intermediates through an initial ET. In a stepwise ET mechanism a radical (or radical ion) intermediate is generated and undergoes a $\sigma$ bond cleavage. Two main dissociation mechanisms are subsequently encountered as seen in Scheme 29 for the dissociation of a radical anion. For a homolytic cleavage, the dissociation takes place with the extra electron remaining on the initial host moiety. Heterolytic cleavage, on the other hand, is associated with an intramolecular ET where the extra electron is transferred to a leaving group across the cleaving bond. The dissociation of radical cations can be similarly understood by changing the signs: heterolytic cleavage also includes an intramolecular transfer to the electron-lacking moiety. It is well accepted that the heterolytic mechanism can be successfully described by extending the DET model. Savéant demonstrated that homolytic cleavage can also be described by a closely related model as will be discussed below.[76,185,284,469,542]

### 6.1.1. Heterolytic Cleavage

It has long been accepted that an intramolecular ET is involved in the heterolytic cleavage of radical ions. It was successfully modeled using an extension of the DET theory,[76,185,284,469,542] which is also applicable to the reverse reaction consisting of an association of a radical and a ion. An activation free energy-driving force quadratic relationship, similar to the one used for intermolecular and heterogeneous DET, was developed (eq 31). The main difference is the contribution, to the intrinsic barrier, of the cleavage reaction ($\Delta G^{\ddagger}_{0,\mathrm{cleavage}}$) of the BDE of the cleaving bond at the radical ion level ($D_{\mathrm{RX}^{\bullet-}}$) instead of the neutral molecule (eq 32).

$$\Delta G^{\ddagger}_{cleavage} = \Delta G^{\ddagger}_{0,cleavage}\left(1 + \frac{\Delta G^{0}_{cleavage}}{4\Delta G^{\ddagger}_{0,cleavage}}\right)^2 \qquad (31)$$

$$\Delta G^{\ddagger}_{0,\mathrm{cleavage}} = \frac{\lambda_0 + D_{\mathrm{RX}^{\bullet-}}}{4} \qquad (32)$$

The BDE at the radical ion level (in other words the cleavage reorganization energy $D_{\mathrm{RX}^{\bullet-}}$) is provided by eq 33, where $D_{\mathrm{RX}}$ is the bond dissociation of the cleaved bond R−X in the neutral molecule (RX), $E^{\circ}_{\mathrm{RX/RX}^{\bullet-}}$ is the standard reduction potential of RX, $\bar{S}$ is the partial molar entropy, and $(\mathrm{R}^{\bullet})^{\bullet-}$ corresponds to an excited state of the carbanion ($\mathrm{R}^{-}$) resulting from the injection of one electron into the LUMO of the radical $\mathrm{R}^{\bullet}$:

$$D_{\mathrm{RX}^{\bullet-}} = D_{\mathrm{RX}} + E^{\circ}_{\mathrm{RX/RX}^{\bullet-}} - E^{\circ}_{\mathrm{R}^{\bullet}/(\mathrm{R}^{\bullet})^{\bullet-}} + T(\bar{S}_{\mathrm{RX}} - \bar{S}_{\mathrm{RX}^{\bullet-}} + \bar{S}_{(\mathrm{R}^{\bullet})^{\bullet-}} - \bar{S}_{\mathrm{R}^{\bullet}}) \qquad (33)$$

The entropic term can be neglected since $\bar{S}_{\mathrm{RX}} - \bar{S}_{\mathrm{RX}^{\bullet-}}$ and $\bar{S}_{(\mathrm{R}^{\bullet})^{\bullet-}} - \bar{S}_{\mathrm{R}^{\bullet}}$ may be seen as canceling each other. The result is that the intrinsic barrier can be written as a function of the BDE of the cleaved bond at the initial neutral molecule which is more accessible as shown in eq 34.

$$\Delta G^{\ddagger}_{0,\mathrm{cleavage}} = \frac{1}{4}(D_{\mathrm{RX}} + E^{\circ}_{\mathrm{RX/RX}^{\bullet-}} - E^{\circ}_{\mathrm{R}^{\bullet}/(\mathrm{R}^{\bullet})^{\bullet-}}) + \frac{\lambda_0}{4} \qquad (34)$$

The solvent reorganization term $\lambda_0$ can be obtained using the Marcus expression (eq 7–9, section 4.1)

The standard free energy of the cleavage reaction can be written as

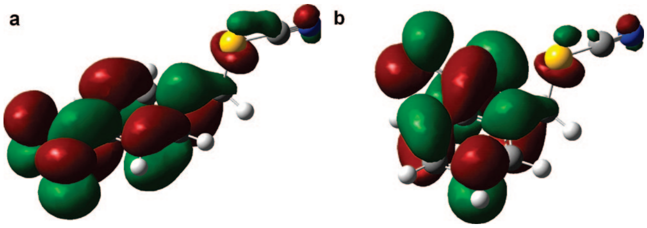



**Figure 20.** LUMOs of (a) 4-nitrobenzyl thiocyanate and (b) 2-nitrobenzyl thiocyanate.

$$\Delta G^{\circ}_{\text{cleavage}} = E^{\circ}_{\text{RX/R}^\bullet+\text{X}^-} + D_{\text{RX}} - E^{\circ}_{\text{X}^\bullet/\text{X}^-} - T\Delta S_{\text{RX/R}^\bullet+\text{X}^\bullet} \quad (35)$$

Many aspects of this extension of the dissociative ET theory to the case of the heterolytic cleavage of radical ions have been analyzed for various series of organic compounds.[76,185,284,469,542]

**Aryl Halides.** In an initial study, Savéant's model, as described above for the formation/dissociation of radical ions, was applied to the reductive cleavage of a series of aryl halides.[76] Since the kinetic data were available for these compounds from previous studies[74,75] it was possible to readily obtain the activation−driving force plots for the aryl chloride and aryl bromide series as well as to compare experimental and predicted values of the intrinsic barrier for the cleavage reaction. Equation 35 was used to obtain $\Delta G^{\circ}_{\text{cleavage}}$ since all the required parameters were available and the activation free energy was obtained from the experimentally determined rate constants using eq 36:

$$\Delta G^{\ddagger}_{0,\text{cleavage}} = \frac{RT}{F}\ln\left(\frac{k_{\text{B}}T}{hk}\right) \quad (36)$$

Both aryl chlorides and bromides showed a linear variation of the activation energy with the driving force, with a slope close to 0.5. Intrinsic barrier values were deduced through linearization of the quadratic relationship. For aryl chlorides and aryl bromides the experimental values were found to be equal to 0.41 and 0.39 eV, respectively. Intrinsic barrier values were also predicted through application of the model. In the initial study, the predicted values using eq 34 were larger (1.23 and 1.03 eV). Later studies took advantage of the inclusion of out-of-plane bending in the dissociation of aromatic halides (as discussed below)[77] and also more recently of the availability of additional kinetic data for related compounds.[682–684]

**Nitro-Substituted Benzyl Thiocyanates.** Another recent example is the electrochemical reduction of nitro-substituted benzyl thiocyanates[31] which leads to the cleavage of the $CH_2$−S bond (α-cleavage). On the other hand similar compounds containing electron-donating or weak electron-withdrawing groups lead to the dissociation of the S−CN bond (*β*-cleavage) (section 4.5). The LUMOs of the nitro-substituted benzyl thiocyanates are located on the nitrophenyl moiety with a lower participation of the rest of the structure (Figure 20). The electrochemical data and the theoretical calculations provided detailed information about the radical anion intermediates resulting from the one electron reduction of the nitro-substituted compounds in a stepwise ET mechanism. Savéant's theory for the dissociation of radical ions was successfully applied to support the experimental data showing that the cleavage of the $CH_2$−S chemical bond in these intermediates is the favored pathway rather than the S−CN bond cleavage, from both a kinetic and a thermodynamic point of view. The thermodynamics of the intramolecular heterolytic ET can be described by eq 37:

$$\Delta G^{\circ} = E - E^{\circ}_{\text{RX/R}^\bullet+\text{X}^-} = E + D_{\text{R-X}} - E^{\circ}_{\text{X}^\bullet/\text{X}^-} - T\Delta S_{\text{RX/R}^\bullet+\text{X}^\bullet} \quad (37)$$

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

Knowing the BDEs 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), the thermodynamics of the two processes were able to be compared. The standard oxidation potential of cyanide ($E^{\circ}_{\text{CN}^\bullet/\text{CN}^-} = 2.25$ V/SCE) and that of thiocyanide ($E^{\circ}_{\text{NCS}^\bullet/\text{NCS}^-} = 0.65$ V/SCE) are both known.[31] While the big difference (1.6 V) between the oxidation potentials of the two leaving groups clearly favors a *β*-cleavage, this advantage is totally compensated for by the huge difference between the bond dissociation energies (≅50 kcal/mol or 2.16 eV) through favoring the α-cleavage. This confirms that from a thermodynamic point of view the α-cleavage is more favorable than the *β* one.

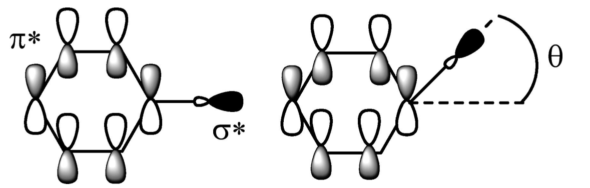
From a kinetic point of view, the intrinsic barrier for the decomposition of potential radical anions involves the dissociation energy of the cleaved bond at the level of the radical anion. Because the $\pi^*$ orbital of the aryl moiety is the electron-hospitable orbital in the reduction (Figure 20), the dissociation follows a heterolytic cleavage. The contribution of the bond dissociation to the intrinsic barrier of the decomposition of the radical anions of nitro-substituted benzyl thiocyanates is described by eq 34. This result shows a total independence on the oxidation potential of the leaving group. This is the only factor that would favor the *β*-cleavage over the α one. $E^{\circ}_{\text{O}_2\text{NBn}^\bullet/(\text{O}_2\text{NBn}^\bullet)^{\bullet-}}$ and $E^{\circ}_{\text{O}_2\text{NBnS}^\bullet/(\text{O}_2\text{NBnS}^\bullet)^{\bullet-}}$ would not be very different since they both represent the injection of one electron in the $\pi^*$ orbital of the nitro phenyl moiety. In addition, the solvent reorganization energy would not be very different for the two dissociation modes (α and *β*). If they were, the solvation reorganization energy would be expected to be slightly larger for *β*-cleavage since it leads to a smaller anion ($CN^-$). In this case the BDE, which favors an α-cleavage, is the predominant factor.

In conclusion, it can be demonstrated that application of Savéant's theory to the dissociation of the radical anions of nitro-substituted benzyl thiocyanates permits a rationalization of the experimental data. It shows that the α-decomposition of a potential radical anion, within this series of compounds, is favored over the *β* one from both a thermodynamic and a kinetic point of view.

**Role of Bending and Cluster Formation in the Dissociation of Radical Ions.** *Aromatic Radical Ions.* Haloaromatic radical anions present a symmetry restriction when it comes to the intramolecular transfer of an electron from the SOMO $\pi^*$ orbital to the carbon−halogen $\sigma^*$ orbital due to the absence of overlap resulting from the planner structure (Scheme 30).

This symmetry restriction in the planar geometry of aromatic halides has been long recognized.[283,284,542,628,673,675,685,686] Out-of-plane bending was in fact suggested as one way to overcome this geometry restriction.[74,687] This was further supported both theoretically[688] and experimentally[689] by subsequent studies in the gas phase. But it was not until recently that Hynes and

**Scheme 30**




coworkers were able to extend the model to take this rearrangement into consideration thus allowing an estimation of the energy change on bending the C−halogen bond out of the aromatic ring plane in the transition state. In the planar configuration only the C−Cl distance is elongated. Hynes et al. used 4-chlorobenzonitrile as a model in their theoretical treatment of the dissociation of aromatic radical anions.[684,690,691] Their formulation was based on an approach similar to the DET theory as applied to the formation/dissociation of radical ions. This is based on a Morse potential curve for the reactants and a dissociative Morse curve for the products. It also included the contribution of the bending of the cleaving bond and the related electronic coupling. This was achieved through the addition of the same harmonic potential ($k_\theta\theta^2/2$) for the newly introduced bending coordinate to both potential surfaces (eq 38). $\theta$ is the bending angle between the C−Cl bond and the aromatic ring plane, and $k_\theta$ is the associated force constant.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta G^0}{4\Delta G_0^{\ddagger}}\right)^2 + k_\theta\theta^2/2 \qquad (38)$$

One of the assumptions made is the purely harmonic nature of the potential along the coordinate ($\theta$), and this was supported by the fact that the angle remains small (<30°). The introduction of a quadratic component proved unnecessary, as it would dominate only for large angle values. It was also assumed that the force constant was the same for both reactants and products and was independent of any cleaving bond variation going from the equilibrium state in the reactant to the transition state. The bending induces electronic coupling ($\beta$) between the $\pi^*$ orbital which initially hosts the electron, and the $\sigma^*$ orbital of the C−Cl bond undergoing cleavage. This electronic coupling is assumed to depend solely and linearly on the bending angle $\theta$ ($\beta(\theta) = b\theta$). Key parameters were thus obtained from electronic structure calculations for the vacuum adiabatic surfaces and optimized through comparison with the diabatic representation.[684,690,691]

The resulting gas phase potential energy surfaces obtained for 4-chlorobenzonitrile in Figure 21 provided a better conceptualization of the conical intersection that is unavoidable if the bending of the C−Cl bond is not considered. Out-of-plane bending induces a finite electronic coupling and hence shifts the transition state out of the conical intersection, thus allowing ET from the $\pi^*$ to the $\sigma^*$ orbital.

Further application to the dissociation of 4-chlorobenzonitrile in solution required consideration of solvation effects. A dielectric continuum solvent model was used to address a nonequilibrium solvation situation where the solvent polarization is not continuously in equilibrium with the charge distribution of the fast cleaving radical anion as the reaction proceeds.

An important feature of the introduction of the out-of-plane bending is its effect on the dynamics of the dissociation process. The increase in energy required for the required

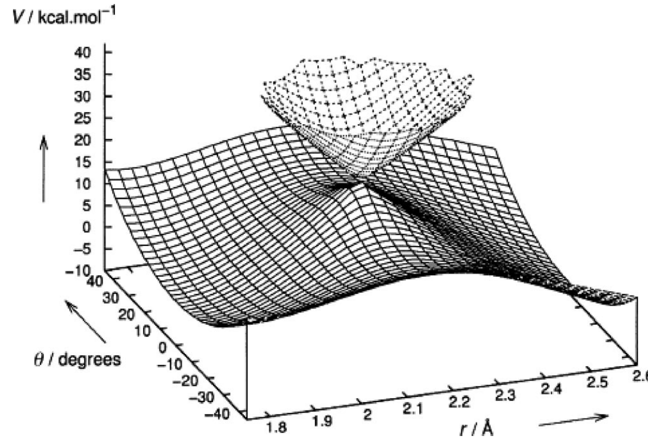



**Figure 21.** Gas phase potential energy surfaces for the 4-chlorobenzonitrile radical anion. The reaction coordinates are the C−Cl bond length ($r$) and the bending angle ($\theta$). Reprinted with permission from ref 690. Copyright 2003 American Chemical Society.

bending of the C−Cl bond is overcompensated for by stabilization through electronic coupling which results from the induced orbital overlap. For 4-chlorobenzonitrile, a net decrease in the transition state free energy, compared to the conical intersection energy, was estimated as around 8 kcal/mol.

More recently, the dissociation of aryl chlorides and aryl bromides has been revisited.[77] In addition to the inclusion of the C−Cl bond bending to avoid conical intersection at the transition state, as discussed above, another important factor was introduced in order to take into account the intermediate formation of a $\sigma$ radical anion or an ion/radical cluster en route to the total dissociation of the $\pi$ initial radical anion. Examples that have been shown to involve such behavior include the reduction of 4,4′-dinitrodiphenyl disulfide[65] and, more recently, two nitrophenyl sulfenyl chlorides as discussed below.[82] The intermediate formation of such radical/anion clusters, during the dissociation of the corresponding $\pi$ radical anions, has also been confirmed through recent quantum calculations.[683] A new expression that is similar to eq 38 was thus obtained for $\Delta G^{\ddagger}_{0,\mathrm{cleavage}}$. However, the BDE has been replaced by the term $(\sqrt{D_{RX\bullet-}} - \sqrt{D_{R\bullet,X-}})^2$, which is similar to the one used in the "sticky" DET theory.[571–577] The difference is that this term includes the BDE of the cleaved bond at the level of the radical anion and not the neutral structure. Introduction of factors related to out-of-plane bending and cluster formation considerably reduces the predicted intrinsic barrier so that it becomes compatible with the experimental one. The validity of this new expression was extended to the dissociation of radical anions corresponding to series of bromo- and chlorobiphenyls as well as bromonaphthalenes[77] for which the rate constants had been recently determined using pulse radiolysis.[683]

The Hynes model was also successfully applied to the homolytic fragmentation of the N−O bond for a series of $N$-methoxypyridyl radicals[692] (see section 6.2).

*2-Nitro- and 2,4-Dinitrophenyl Sulfenyl Chlorides.* As discussed in section 4.5, the electrochemical study of these two compounds suggested that their reduction follows a stepwise ET mechanism with a radical anion as an intermediate. Theoretical calculations supported this idea as they showed that the LUMOs are more delocalized over the nitro-substituted aryl moiety. This indicates that the incoming

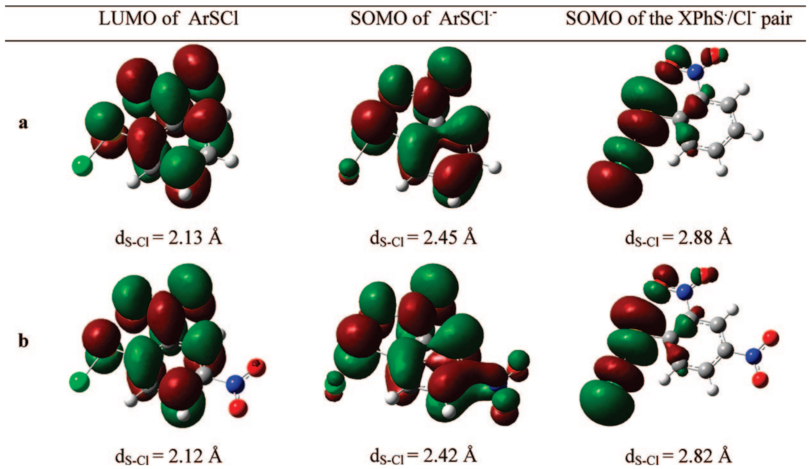
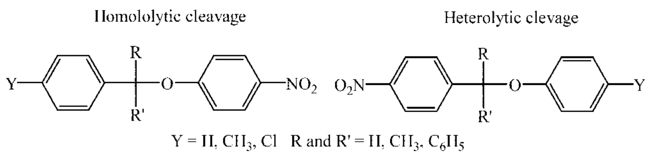



**Figure 22.** LUMOs and SOMOs of 2-nitrophenyl sulfenyl chloride (a) and 2,4-dinitrophenyl sulfenyl chloride (b) and their reduced forms, respectively. Adapted with permission from ref 83. Copyright 2006 American Chemical Society.

**Chart 5**



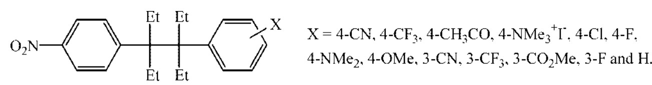

electron would be injected into the $\pi^*$ orbital thus yielding a radical anion intermediate. Radical anions are in fact obtained for these compounds and their SOMOs are also delocalized over the nitro-substituted aryl moieties as seen in Figure 22. These radical anions are observed at S−Cl distances in agreement with the formation of a $\pi$ radical anion. Interestingly, another minimum is obtained for the reduced form for both compounds. These minima are observed at longer S−Cl distances, similar to those observed for other compounds within the series (see section 4.5). These have been shown to undergo a "sticky" DET[83] involving the formation of radical ion pairs rather than "real" radical anions. For these intermediates the electron density is totally located on the S−Cl bond, indicating that the radical anions formed through a stepwise ET mechanism on reduction of the parent compounds (2-nitro- and 2,4-dinitrophenyl sulfenyl chlorides) yield the corresponding radical/ion pairs before falling apart. This provides a good example of cluster formation through the dissociation of a radical anion. Similar behavior yielding a $\sigma^*$ radical anion from an initially formed $\pi^*$ radical anion is found in the reduction of di-4-nitrophenyldisulfide.[65]

### *6.1.2. Homolytic Cleavage*

The homolytic cleavage of radical ions, the associated kinetics and thermodynamics and the difference in dynamics compared to heterolytic cleavage have all attracted considerable attention.

The kinetics of the homolytic dissociation of the radical anions of 4-nitrophenyl benzyl ethers (Chart 5) generated through homogeneous ET using the 2,4,6-tributynitrobenzene radical anion as a donor was studied in detail using ESR.[6] The dissociation of the C−O bond in this series has been shown to be exothermic. A comparison with the dissociation of the C−O bond in radical anions in a series of 4-nitrobenzyl phenyl ethers (Chart 6), which in fact follows heterolytic cleavage, provides interesting insights. While the dissociation of the radical anions in both series provides a benzyl radical

**Chart 6**




and a phenoxide anion, that of the former radical anions possesses a larger driving force. This thermodynamic advantage was, however, accompanied by a kinetic disadvantage, since the dissociation was at least 4 orders of magnitude slower. This has been explained in terms of the extra intrinsic barrier for the homolytic cleavage reaction resulting from a non-regioconservation of the spin density. It was suggested that dissociation reactions of radical anions that occur with a regioconservation of spin density are in fact kinetically preferred. This is the case for 4-nitrobenzyl phenyl ethers, where fragmentation yields a nitrobenzyl radical and a phenoxide anion and the spin density is preserved throughout the process. To provide further support for this hypothesis, the dissociation of radical anions of series of naphthylmethyl phenyl ethers and naphthyl benzyl ethers, generated through homogeneous ET using the radical anions of anthracene and fluoranthene, were investigated.[7] Here again, the latter radical anions, which undergo an exothermic homolytic cleavage, showed dissociation rate constants that were much slower than the former ones, undergoing a heterolytic cleavage. The thermodynamics of the two processes have been suggested not to differ much with a potential slight advantage for the dissociation of the naphthylmethyl phenyl ethers undergoing the heterolytic cleavage.

Subsequent studies involving the cleavage of relatively nonpolar C−C bonds provided more insight into the dynamics of homolytic vs heterolytic cleavage in the dissociation of radical anions[8−11] and radical cations.[140] In particular, the dissociation of radical anions of 1-(4-nitrophenyl)-2-(substituted-phenyl)-1,1,2,2-tetraethylethanes (Chart 6) was discussed in terms of activation of the scissile bond and of the charge delocalization across this bond in the transition state.[11] All compounds dissociate to the 3-(4-nitrophenyl)-pentyl anion and the 3-(substituted-phenyl)-pentyl radical. The electron is initially injected into the nitro-aryl moiety, and the dissociation has been described as being kinetically dependent on the ability of the charge to be delocalized across the cleaving bond. A similar interpretation, implicitly involving intramolecular ET, was also formulated to explain the dissociation of polar C−O bonds in ethers.[32] Intramolecular ET was also considered in studies of dissociative electron attachment to alkyl chlorides.[693,694] In a more fundamental approach, Savéant described this type of homolytic dissociation process in a way similar to the heterolytic one.[76,284] The same quadratic driving force−activation energy relationship (eq 31) applies. The difference is in the intrinsic barrier expression which in this case involves $E°_{X^\bullet/(X^\bullet)^{\bullet-}}$ and the entropy variation (eq 39). Here $(X^\bullet)^{\bullet-}$ represents an excited state of the anion $X^-$ that results from the injection of an electron into the low lying $X^\bullet$ orbital. This equation is also applicable to the reverse reaction consisting of a recombination of an anion and a radical to give a radical anion. $\bar{S}_{(X^\bullet)^{\bullet-}}$ and $\bar{S}_{X^-}$ can be considered as similar since the relaxation energy of $(X^\bullet)^{\bullet-}$ to $X^-$ is negligible in many cases.

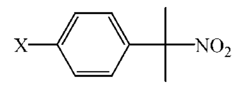
$$G^{\ddagger}_{0,\mathrm{cleavage}} = \frac{1}{4}[D_{RX} + E°_{RX/RX^{\bullet-}} - E°_{X^\bullet/(X^\bullet)^{\bullet-}} + T(\bar{S}_{RX} - \bar{S}_{RX^{\bullet-}} + \bar{S}_{(X^\bullet)^{\bullet-}} - \bar{S}_{R^\bullet})] + \frac{\lambda_0}{4} \quad (39)$$

This approach provides a model for the rationalization of the dissociation process and allows the prediction of general expected trends. A weak cleaving bond $D_{RX}$ and a negative standard potential $E°_{RX/RX^{\bullet-}}$ lower the intrinsic barrier and favor both the forward and the reverse reactions.

Many subsequent studies viewed homolytic cleavage reactions in the framework of a similar quadratic relationship. They investigated different aspects of the reaction kinetics dependency on its thermodynamics. Examples studied include extensive series of 1,1,2,2-tetraalkyl-(bis-4-substituted-phenyl)ethanes.[695,696] Here the radical anions that dissociate following a homolytic cleavage showed relatively larger intrinsic barriers. Hence the different modes were expected to differ in the degree of delocalization of the charge in the transition state.[695] Similar trends were observed in another example, which concerned the mesolytic cleavage of the C−S bond in series of nitrobenzyl substituted phenyl sulfides and nitrophenyl substituted benzyl sulfides.[25]

The C−O bond cleavage in the radical anions formed from alkyl aryl ethers has also been widely investigated.[35–41] Some recent studies included structures closely related to those that triggered the initial interest in the homolytic/heterolytic dichotomy. The cleavage was investigated within the framework of intramolecular DET.[33,42] Intrinsic barriers for aryl alkyl ethers following homolytic cleavage reactions ranged from between 0.7 and 0.8 eV, and analysis showed that the main contribution is that from bond dissociation in the radical anion. Solvent reorganization provided only a minor contribution.[42] In another study fragmentations of radical anion series following either homolytic (4-cyanophenyl alkyl ethers) or heterolytic (4-cyanobenzyl methyl and 4-cyanobenzyl phenyl ethers repectively) cleavages were compared.[33] A combination of experimental electrochemical data and theoretical calculations helped rationalize the results. The dissociation was associated with an intrinsic barrier that is on average 3 kcal/mol higher and which is independent of the thermodynamics. 4-Cyanbenzyl phenyl ether showed a dissociation intrinsic barrier 5.5 kcal/mol higher than that of 4-cyanophenyl benzyl ether. Although the latter radical anion fragments more slowly than the former, its thermodynamics were more favorable and hence both cleavages turned out to be exergonic. The kinetics were shown to depend mainly on the characteristics of the transition state $\sigma^*$ orbital around the alkyl-O group. The thermodynamics, on the other hand, depend on the stabilizing effect of the electron withdrawing cyano substituent on the products. This effect is larger for the cyanophenolate anion than for the cyanobenzyl radical, produced through homolytic and heterolytic cleavages, respectively. In such structures, the cyano group favors the homolytic cleavage from a thermodynamic point of view and the heterolytic cleavage from a kinetic point of view.

**Chart 7. Investigated α-Nitrocumenes[698]**

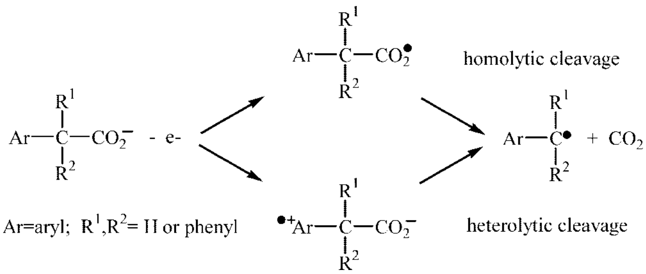


X = H, CN, $NO_2$

Although for most of the previous examples the homolytic cleavage is exothermic, many endothermic processes for the dissociation of both radical cations and radical anions have been reported. In one interesting study, the dynamics of a C−C bond fragmentation in a series of radical cations of tert-butylated NADH analogues were investigated.[12] Rate constants for a variation of the standard free energy in the order of 0.4 eV, varying by 6 orders of magnitude for the dissociation reaction, were measured by cyclic voltammetry and homogeneous redox catalysis. A plot of the variation of the logarithm of the rate constant with the standard free energy was linear with a slope of 1/60 meV. This indicates that it is the diffusion of the two fragments out of the solvent, rather than activation, that controls the kinetics of the fragmentation reaction. Interestingly, further analysis of previously reported kinetic data for endothermic C−C bond fragmentation in a series of bibenzyl radical cations and radical anions showed similar trends.[12] In these systems the intrinsic barrier is small, indicating that internal and solvent reorganization energies are moderate. More recently, the origins of activation barriers in the homolytic cleavage of radicals and radical ions have been rigorously investigated.[697] The activation energy−driving force relationship, similar to that used for the heterolytic cleavage, was obtained through consideration of a two-state semiclassical model. This was based on the intersection of potential energy surfaces characterizing bond dissociation and formation. The potential extension of this model to cases where strong in-cage interactions between fragments are taken into consideration has also been discussed.[697] The analysis shows that the two main contributions to the intrinsic barrier are the triplet excitation energy of the leaving group and the energy of the excitation from the $\pi^*$ to the $\sigma^*$ orbital in the initial radical ion (or radical). This model was tested using a series of 4-cyanophenyl ether radical anions, through comparison of the experimental and predicted activation barriers as a function of the driving force, and good agreement was found.

It has been shown for a series of α-nitrocumenes (Chart 7) that the dissociation mechanism of the radical anion is dictated by the nature of the substituent in the para position of the aromatic ring.[698] While the radical anions of α-nitrocumene and *p*-cyano-α-nitrocumene dissociate following a homolytic cleavage, 4-nitro-α-nitrocumene, on the other hand, follows a heterolytic process. The rate constant of the dissociation of the radical anion of the para nitro compound was 4 orders of magnitude slower than the others. This substantial difference was accounted for in terms of the driving force differences. For the 4-nitro compound, where the electron is injected into the nitro-phenyl moiety, the driving force is much smaller than for the other two compounds. Here the electron is injected into the nitro-alkyl moiety. The potential involvement of an initial intramolecular

**Scheme 31. Mechanism of the Kolbe Reaction of Arylmethyl Carboxylate Ions**



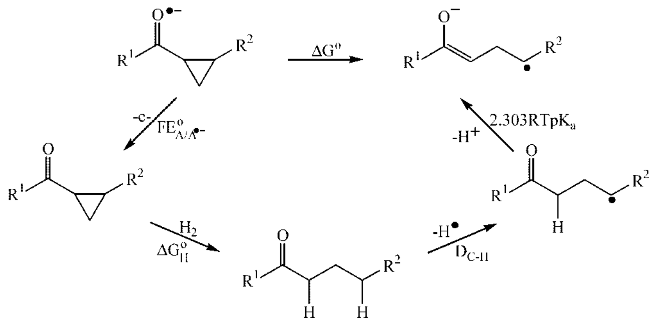

ET step, making the mechanisms similar for all 3 compounds, has also been suggested.[185]

Another interesting example is the cleavage mechanism of the radical intermediates in the anodic oxidation of arylmethyl carboxylate ions.[699] The electrochemical oxidation of carboxylate ions, i.e. the Kolbe reaction, is one of the oldest and best known reactions in eletroorganic synthesis. The mechanism of the initial ET has attracted considerable attention, and while a concerted mechanism has been suggested based on thermodynamic considerations,[700] in a number of studies the reaction has clearly been shown to involve a stepwise initial ET.[699,701,702] Even if earlier photochemical studies indicated that acyloxy radicals can have a finite lifetime,[703] it was only recently that the oxidation of arylmethyl carboxylate ions has indeed been shown, based on cyclic voltammetric data and electrolytic products distribution, to involve the intermediate formation of the corresponding carboxyl radical in a stepwise ET mechanism.[699] This led to the conclusion that the thermodynamic advantage of the concerted pathway was overcompensated for by a high nuclear reorganization. The intermediate arylmethyl oxyl radicals have been shown to undergo a C−C cleavage following either a homogeneous or a heterogeneous mechanism, depending on the nature of the arylmethyl group as shown in Scheme 31.

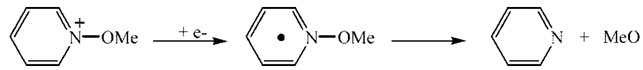
When the arylmethyl group is strongly electron donating, to a point that the oxidation removes an electron from the aryl moiety, the radical generated undergoes a heterolytic cleavage through a slow process. Otherwise, the oxidation leads to an unpaired electron on the carboxylic moiety and the radical cleaves very rapidly following a homolytic mechanism. It should be noted that this difference has an important impact on the overall reaction under electrochemical conditions. The fast homolytic cleavage of the radical favors the "non-Kolbe" reaction since the arylmethyl radical is produced close to the electrode and is therefore immediately oxidized. The slow heterolytic cleavage, on the other hand, favors the Kolbe reaction. Here the parent zwitterionic radical diffuses away from the electrode and yields the arylmethyl radical far away from the electrode, where dimerization can more efficiently compete with the homogeneous oxidation.

In a series of very interesting manuscripts, Tanko and his co-workers extensively investigated the homolytic ring opening of the radical anions of cyclopropyl ketones generated through the one electron reduction of the parent molecules.[13−22] The investigations led to an activation−driving force relationship in agreement with that reported by Savéant.[76,185,284,469,542] They determined the rate constants of the cleavage reactions using either direct electrochemistry or homogeneous catalysis. It was suggested that the dissociation depends on the charge and spin delocalization in

**Scheme 32. Thermochemical cycle used to estimate the driving force, $\Delta G^0$.**




**Scheme 33. One Electron Reduction of Methoxy Pyridinium**




both the reactant (closed radical anion) and product (open distonic radical anion).

As shown in Scheme 32 a thermochemical cycle was proposed and used to estimate the corresponding driving force, $\Delta G°$, leading to eq 40.

$$\Delta G^{o} = FE^{o}{}_{A/A^{\bullet-}} + \Delta G^{o}{}_{H} + D_{C-H} + 2.303RTpK_{a} - C \quad (40)$$

The standard reduction potentials, $E°_{A/A^{\bullet-}}$, were determined using electrochemistry and homogeneous catalysis. The energy of the hydrogenation of cyclopropane, $\Delta G°_H$, the bond dissociation energy of the C−H bond, $D_{C-H}$, and the p$K_a$ values were all estimated. In addition, $C$, which corresponds to the energy of the rest of the reaction to complete the cycle (i.e., the bond dissociation of $H_2$ and the standard oxidation potential $E°_{H^\bullet/H^+}$), was also estimated. This approach has been successfully applied to a wide variety of cyclopropyl ketones for which kinetic and thermodynamic data have been determined.

Equation 41, which is a combination of Eyring equation and the quadratic activation−driving relationship, was used to estimate the driving force.

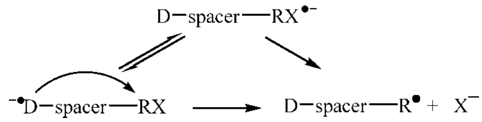
$$\log(k_o) = \log\left(\frac{k_B T}{h}\right) - \frac{\Delta G_0^{\ddagger}}{2.303RT}\left(1 + \frac{\Delta G°}{4\Delta G_0^{\ddagger}}\right)^2 \quad (41)$$

A reasonable agreement was found between the plots of the logarithm of the experimentally determined ring-opening rate constant, as a function of the driving force estimated using both methodologies (thermochemical cycle and quadratic activation−driving force relationship of Marcus type).

Another interesting example is that of the homolytic dissociation of the N−O bond in a series of *N*-methoxypyridyl radicals. Here out-of-plane bending was shown to be as important as in the heterolytic cleavage of the radical anions of aromatic halides.[54−56,692] Indeed the one electron reduction of pyridinium salts has been widely investigated and their reduction has been shown to lead to an intermediate radical which dissociates yielding pyridine and a methoxyl radical, in a stepwise ET mechanism (Scheme 33).[54−56,58,692]

In these reductions, the electron is initially injected into the aromatic ring $\pi^*$ orbital and the formation of the products requires intramolecular ET from the $\pi^*$ orbital to the $\sigma^*$ orbital of the N−O bond which, in the planar radical configuration, is symmetry forbidden. This is circumvented by the out-of-plane bending of the N−O bond. It was

**Scheme 34. Dissociative Intramolecular ET in D−Sp−A Systems**




suggested that, unlike for the aromatic halides, the three electron N∴O bond may not be repulsive as it is less polar. As a result the intermediate formation of $\sigma^*$ radicals is not ruled out. Two main states, $\pi^*\sigma\pi^*$ and $\sigma\sigma^{*2}$ that predominate at shorter and longer distances of the N−O bond respectively, have been discussed and shown to mix readily upon out-of-plane bending of the N−O chemical bond. The activation barriers associated with the cleavage of substituted *N*-methoxypyridyl radicals were determined experimentally, through use of the model and also from DFT calculations, and the three values have been shown to be in good agreement for all compounds investigated. The cleavage reaction has been shown to be faster and more exothermic with electron donating substituents; with the opposite trend for electron-withdrawing substituents. The out-of-plane bending angle and N−O bond length for both the minimum bound radical and the transition state were modeled as a function of the driving force within the series. In both cases the N−O distance and the out-of-plane bending angle increased with the increasing driving force and the variations were larger in the bound state. This results in the bound radical approaching the transition state for the compounds with large driving forces, and therefore the reaction becomes barrierless.

## 6.2. Long Range Dissociative Electron Transfer

In addition to the examples described in the previous section in which the intramolecular ET takes place between a $\pi^*$ orbital and a $\sigma^*$ orbital close to each other or presenting some degree of overlap, other examples have been investigated where the distance between the two centers is larger. They are separated by a molecular spacer (Scheme 34). Due to their fundamental, as well as practical, importance, there is presently an increasing interest in studying such systems. In investigating the dynamics of this type of ET reaction, advantage can be taken of the accumulated data regarding the wide range of structures that can be used as intramolecular donors or acceptors.

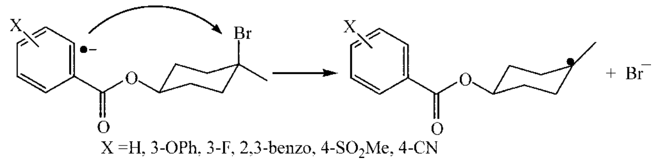
Just as for heterogeneous and intermolecular homogeneous ET reactions, two mechanisms need to be considered in the present case. In the stepwise mechanism, the electron, initially hosted by the $\pi^*$ orbital of the donor, is transferred into a $\sigma^*$ orbital in the acceptor to yield a new radical anion that subsequently undergoes a bond dissociation. The dissociation follows either a homolytic or a heterolytic mechanism as seen in the previous section (6.1). The other mechanism is the concerted process where the ET and bond cleavage are simultaneous.

### *6.2.1. Concerted Intramolecular Dissociative Electron Transfer*

Recent studies have provided interesting insights into the dynamics of concerted intramolecular dissociative ET within custom-designed systems.

As shown in Scheme 35, the intramolecular ET between substituted aromatic benzoates and a tertiary alkyl bromide

**Scheme 35. Intramolecular ET between Substituted Aromatic Benzoates and a Tertiary Alkyl Bromide**



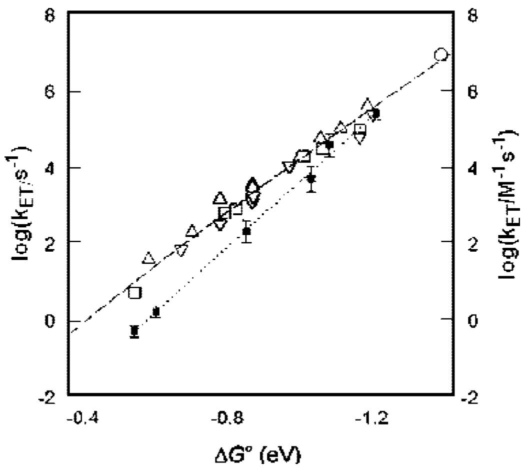




**Figure 23.** Plot of the logarithm of the first-order intramolecular (■) and the second-order intermolecular (□, ○, Δ, ∇) ET rate constants for the reduction of tertiary bromides against the reaction free energy. Adapted with permission from ref 649. Copyright 1998 American Chemical Society.

group through a cyclohexyl spacer was investigated by electrochemistry with the help of convolution analysis.[649] The use of this tertiary alkyl bromide as an electron acceptor was dictated by the availability of extensive data regarding the reduction of the parent *tert*-butyl bromide.[68,251,260,564] The electrochemical reduction of 4-*tert*-butyl-1-methylcyclohexyl bromide, which is structurally similar to the spacer-RX group, was performed nevertheless and its standard reduction potential was determined using convolution analysis. Intramolecular ET rate constants were experimentally estimated, through cyclic voltammetric and homogenous catalysis studies, for different substituted benzoates as donors (Scheme 35). The free energy effect was analyzed. The intermolecular ET through electrochemical homogeneous catalysis using similar donors (providing a driving force window between 0.5 and 1.2 eV) was also investigated. These data were compared, and while both sets showed a linear dependence with the driving force, it was found that the intramolecular ET rate constant was more sensitive to the driving force changes (Figure 23). This difference also translated into differences in the corresponding deduced transfer coefficients.

This difference was explained in terms of the effect of the substituent between the two electroactive centers in the parent structures. In addition to the decrease in the driving force induced on introducing a stronger electron-withdrawing substituent, there was also a change in the center of the SOMO orbital. This led to an increase in the effective distance to the acceptor (C−Br) and a weakening of the ensuing electronic coupling. The rate constant was discussed in terms of the general nonadiabatic ET expression (eq 42),[704,705] and the effects of the distance between the two centers and the reorganization energy were discussed.

$$k = A \exp(-\beta(d - d_0)) \exp(-\Delta G^{\ddagger}/RT) \qquad (42)$$

where the pre-exponential factor ($A = Z\kappa_{el}$) depends on the

**Scheme 36**

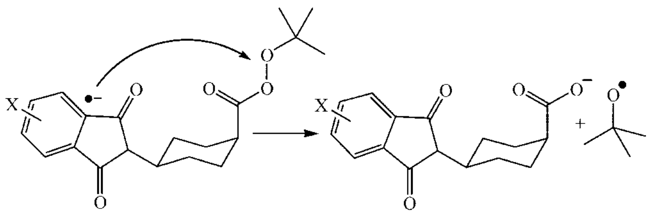
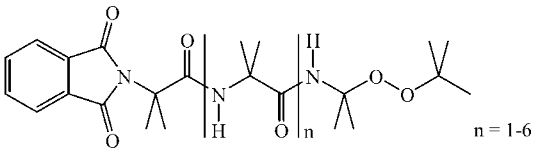



**Chart 8**




effective frequency for motion along the reaction coordinate ($Z$) and the electron transmission coefficient ($\kappa_{el}$) at the van der Waals distance space between the two center $d_0$. The ET distance is $d$, and $\beta$ is the exponential decay parameter.

Further support for these results came from the investigation of a series of similar systems by the same group. They used a substituted phthalimidyl moiety as the donor, and a peroxide group was the acceptor undergoing concerted ET (Scheme 36).[283,650]

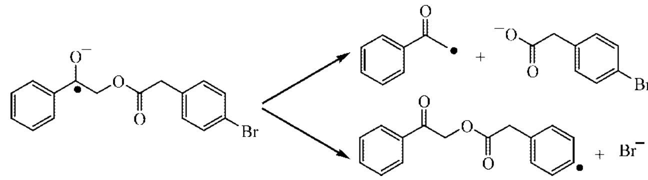
One interesting result from this study was the fact that the center of the SOMO does not change much with the nature of the substituent except for the nitro group as shown by ab initio calculations. The intramolecular ET rate constant in this series was shown to be slightly less sensitive to the driving force changes than the intermolecular reaction. This difference was explained through the involvement of larger intrinsic energy barriers resulting from the higher reorganization energies associated with the intramolecular ET reactions. The nitro-derivative, on the other hand, showed a similar behavior to the previous series in the sense that the increase of the effective distance between the two centers resulted in a considerably slower ET. The electronic coupling between the two centers was studied using the approach developed by German and Kuznestov[530–533] for nonadiabatic ET. They expressed the pre-exponential $A$ in eq 42 as a function of the electronic coupling, $H_{DA}$ (eq 43):

$$k = \left[2\pi {H_{DA}}^2/\sqrt{16\pi RT\Delta G_0^{\ddagger}\exp(-2\beta(d-d_0))}\right]\exp(-F\Delta G^{\ddagger}/RT) \quad (43)$$

Using experimental rate constants, the electronic coupling between the donor and acceptor for both intermolecular and intramolecular ET reactions was investigated. The estimated electronic coupling between the donor and acceptor within the parent structures for the intramolecular ET was indeed shown to be a lot weaker than that for intermolecular ET. Examination of the rate constant as a function of the temperature provided a similar value for the electronic coupling as well as a value for the intrinsic barrier ($\Delta G_0^{\ddagger}$). This was in good agreement with the one determined from the reorganization energy using the Marcus theory.

Another interesting study[651] provided insights into the role of the biologically relevant bioorganic spacers, α-aminoisobutyric acid homooligomers, in the intramolecular ET between similar electroactive centers (a phthalimidyl radical anion moiety and a peroxide group (Chart 8). Nondissociative ET through peptide spacers has been reported emphasizing the importance of the distance between the donor and acceptor[706–718] because the rate constant tends to decrease exponentially with the distance.

**Scheme 37**




Intriguingly, the intramolecular ET within the structure shown in Chart 8 was found to be faster as the number of amino isobutyric (Aib) units increased from 1 to 3 and then almost independent of the distance as the number increased further. This unique behavior, compared to that observed for peptide spacers,[706–718] was accounted for by considering the important role of intramolecular hydrogen bonding interactions that appear to counterbalance the negative effect of distance. This can be attributed to the fact that Aib peptides have a tendency to form rigid structures. The importance of hydrogen bonding in intramolecular nondissociative ET through peptide bridges had in fact been previously identified.[647,648,719,720]

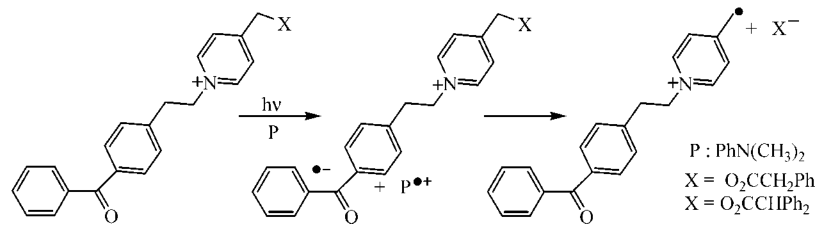
More recently, such systems were investigated using computational techniques.[652–654] Using eq 43 all the necessary parameters were computed using the density functional theory, its time dependent extension and the polarizable continuum model.[652–654] Computed intramolecular ET rates constants were shown to be in agreement with the experimental ones. The importance of the orientation of both donor (phthalimide) and acceptor (peroxide) groups within the structure, the nature of the substituent on the peroxide, and the role of the solvent have all been discussed.

### 6.2.2. Stepwise Intramoleular Dissociative ET

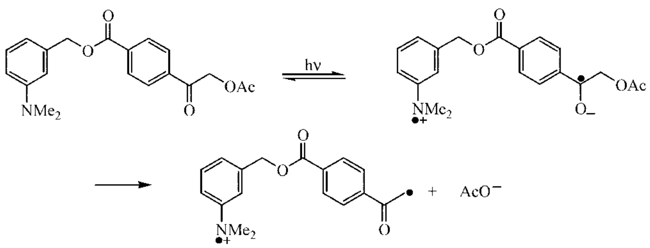
Further interesting examples that have been studied are mainly in the general context of the photochemical release of functional groups. These photoremovable protecting groups (PRPGs) are linked to a key functional group within a molecule in order to deactivate it toward specific reactions, thus providing a new way to phototrigger inherently nonphotochemical reactions.[721–725] From a practical point, interest in these systems is driven by their use in synthesis,[726] the investigation of enzymatic[727] and cellular processes,[728] and in combinatorial chemistry.[729,730] Interestingly, PRGSs have been designed so that the release process is based on a photoinduced intramolecular dissociative ET.[102,605,655] Thus systems have been designed where a photosensitizer was attached through a molecular bridge (termed protector) to a leaving functional group.[656,657] Under photochemical irradiation the excited sensitizer transfers an electron to an acceptor group within the molecule, causing the dissociation of a $\sigma$ bond. An interesting example is that encountered in the photosensitized release of carboxylates from phenacyl esters.[656] The radical anion of the phenacyl ester of 4-bromophenyl acetic acid (Scheme 37) follows two reactive pathways: the heterolytic cleavage of the C−O bond and the long-range intramolecular dissociative ET leading to the cleavage of the C−Br bond at the end of the molecule.

A similar process uses an electron donor mediator. Under photochemical irradiation, an electron is transferred to a chromophore (termed ET cosensitization[506]) in the PRPG leading to the intramolecular dissociative ET. Scheme 38

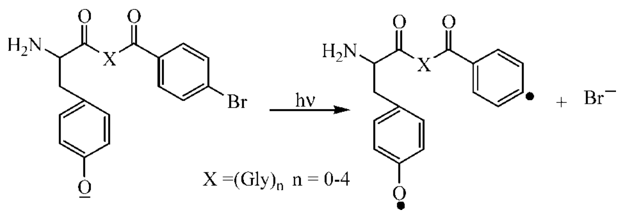
**Scheme 38**




**Scheme 39**



**Scheme 40**




shows an interesting example where the intramolecular donor is benzophenone and the leaving group is a carboxylate.[658]

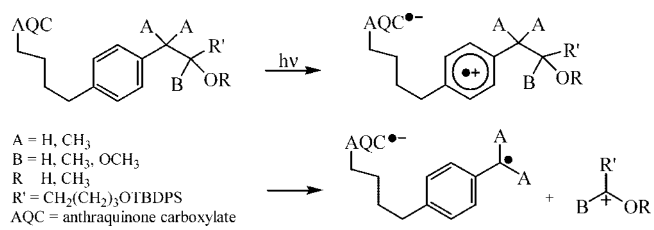
Cosensitization is suggested as a good alternative for avoiding back ET which has been found to be very competitive in closely related systems.[659] In the latter study, the photochemically initiated ET from a *N,N*-dimethylaniline chromophore covalently linked to a phenacyl ester of acetic acid, resulted in the release of acetic acid (Scheme 39).[659] The reaction has been shown to proceed through the intermediate formation of an intramolecular charge-transfer state with a lifetime of approximately 500 ns. The charge-transfer state undergoes either a bond scission, yielding acetic acid or a charge-recombination (back ET) generating the parent ground-state reactant. Investigation of a similar system using anthracene as the chromophore did not lead to the dissociation.

Another interesting example is that shown in Scheme 40 and where the ET between centers separated by peptidic spacers of different lengths has been reported to take place through a stepwise ET mechanism.[660] First, a radial anion at the bromophenyl moiety is generated. It then dissociates following a heterolytic cleavage mechanism.

Another example was recently reported where the donor is the anthraquinone carboxyl group, whose photooxidation induces an intramolecular DET (Scheme 41).[731] The dissociation yield was as high as 97%, and the study showed that either a tertiary alcohol or alkyl substituent at the benzylic carbon speeds up the reaction and increases the dissociation yield. This is because they weaken the benzylic carbon−carbon bond and stabilize the fragments generated.

The more examples of systems involving long-range intramolecular DET that become known, the more pertinent an in-depth fundamental analysis is relevant.

**Scheme 41**




## 7. Single Electron Transfer (SET)/S$_N$2 Dichotomy

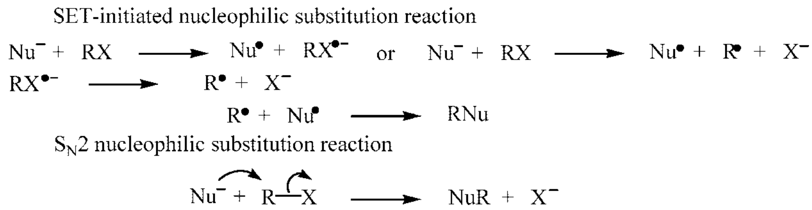
Single electron transfer (SET) processes have also been shown to take place, at least in a competitive manner, in reactions traditionally believed to proceed exclusively through displacement of pairs of electrons. One particular example that attracted considerable attention is that regarding the dichotomy between SET and nucleophilic substitution through the S$_N$2 mechanism. As shown in Scheme 42, a reaction between a nucleophile ($Nu^-$) and an electrophile such as an alkyl halide (RX) can lead to the substitution product (RNu), either through a polar mechanism where a pair of electrons is transferred via nucleophilic attack, or through a SET followed by recombination of the two radicals generated ($R^\bullet$ and $Nu^\bullet$). The ET can follow either a concerted or a stepwise mechanism. In many cases, unraveling the mechanism of the nucleophilic substitution has been shown to be a challenging task, and as a result, the dichotomy between the two pathways has been widely investigated from both the experimental and theoretical standpoints.

### 7.1. Experimental studies: SET/S$_N$2 Dichotomy

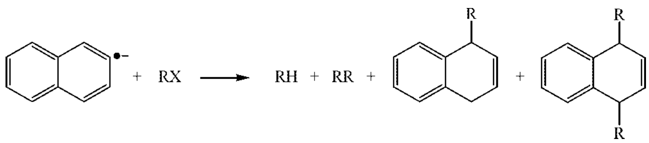
In pioneer work by Kornblum and his co-workers concerning the S$_{RN}$1 reaction, a single ET has clearly been identified as the initial step in the nucleophilic substitution of nitro-substituted benzyl chlorides with 2-nitropropane and 2-carbethoxycoumarane-3-one anions.[732–734] Using the latter nucleophile, the authors investigated the extent of the competition between the SET and the S$_N$2 pathways. They did this through the addition of different electron acceptors such as hexafluorobenzene, nitrobenzene, *p*- and *m*-dinitrobenzene, cupric chloride and sulfate.[733,734] It has been shown that, while, in the absence of an electron acceptor, the major product for the reaction with 4-nitrobenzyl chloride is the C-alkylation product, the O-alkylation product, generated through a S$_N$2 reaction, results when an electron acceptor is added. With $CuCl_2$ the selectivity is particularly striking: the yields change from 90% and 2% to 45% and 48%, for the C- and O-alkylation products, respectively.[734] The authors concluded that the S$_N$2 pathway becomes more and more predominant because the presence of a good electron acceptor suppresses the ET to nitrobenzyl chloride.

Over the last few decades, the S$_N$2 mechanism has been questioned in many nucleophilic substitution reactions at the expense of a mechanism involving a SET initiation. A range

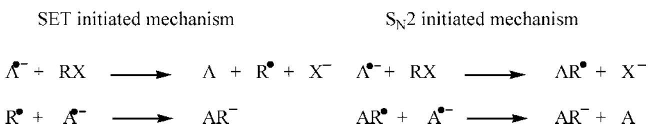
**Scheme 42**



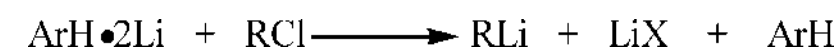
**Scheme 43**



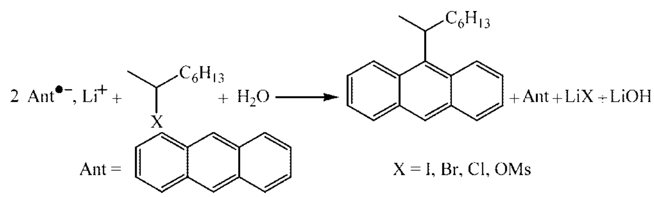
**Scheme 44**



**Scheme 45**



**Scheme 46**



of electron-rich species have been used as nuclophiles and/or electron donors including radical anions, anions, dianions and reduced forms of metals. These were generated chemically, electrochemically, photochemically and by pulse radiolysis. Mechanistic analyses were based on product ratios, kinetics and stereochemical studies. The effects of factors such as the nature of the leaving group, steric hindrance of both reactants and the driving force associated with the reaction have all been investigated. Despite the controversy concerning some specific reactions, it has been established beyond any doubt that SET is an important mechanistic pathway in many nucleophilic substitution reactions, and much of the detail of this dichotomy has been understood.

The reactions of alkyl halides with aromatic radical anions, generated as ion pairs with alkali metals, were among the first to be investigated. Both a SET and a $S_N2$ polar pathway have been proposed.[197,735–743] Naphthalene is one of the most studied radical anions. Its preparation through reduction by alkali metals has been long known, and its ability to act as a good reducing agent[744–747] as well as a Lewis base[746,747] has been well established. Determination of the mechanism, or mechanisms, of its reaction with alkyl halides, and the factors controlling all the potential pathways, have attracted considerable attention.[197,735,736,748–753] These pioneer studies showed that the reaction can lead to different products resulting from alkylation (both monoalkylation and dialkylation), reduction and dimerization reactions.[741,749–751,754,755] (Scheme 43).

While the reduction and the dimerization products have been understandably attributed to a process involving an initial SET, determination of the mechanistic pathway, or pathways, leading to the alkylation products has stimulated an interesting debate. Similar to the case of negatively charged nucleophiles (Scheme 42) is the case of radical anions. The alkylation products may be rationalized by considering either a SET initiation step or a $S_N2$ nucleophilic attack (Scheme 44). The mechanisms differ, however, in that the second step involves the reaction of an alkyl radical with the nucleophile itself and not its oxidized form.

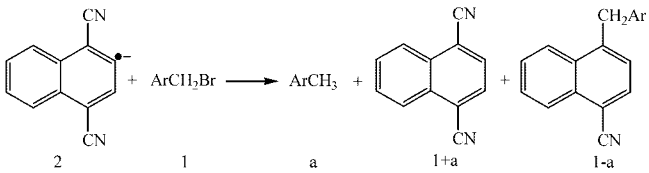
In these early studies, the distinction between the two mechanisms was discussed, in terms of the product ratios and the reaction kinetics. The nondependence of the product ratios on the nature of the halide was seen as an indication of a dominant SET mechanism over the polar pathway.[197]

Recent studies suggested that when alkyl fluorides are reacted with the naphthalene radical anion, the $S_N2$ process is in competition with the SET one. It even becomes the predominant pathway when the naphthalene dianion is employed.[756] It was also suggested that the $S_N2$ pathway is more predominant than the SET pathway for primary alkyl fluorides. The kinetics of the reactions of both the electron rich radical anion and dianion with *n*-, *s*- and *t*-octyl fluorides were investigated. The relative rate constants were determined using competitive kinetic techniques.[757,758] The reactivity has been shown to decrease in the order primary > secondary > tertiary for reactions of octyl fluorides in both the naphthalene radical anion and dianion. This is the opposite of what would be intuitively expected if ET were the main process. With the chlorides, the difference in reactivity was very small.[758] The reactions yielded mainly the reduction product (octane) and the alkylation product. The fact that, with the naphthalene dianion, the 1-fluorooctane yielded 84% of the alkylation product while the 1-chlorooctane yielded 89% of the reduction product led the authors to conclude that the predominant process is the $S_N2$ for the former and the SET pathway for the latter.

An initial SET process has also been suggested in the preparation of organolithium reagents from alkylhalides. In these reactions, lithium and catalytic amounts of an arene are used to form organolithium reagents through an exchange between the halogen and lithium.[759,760] When naphthalene is used, the reaction with a series of organic halides was shown to involve the corresponding dianion (Scheme 45). This acts as an efficient electron donor. Kinetic analysis suggested that this process dominates over both the ET from the naphthalene radical anion and the $S_N2$ pathway.[761]

Besides the product ratios, stereochemical analysis has also been used to discriminate between the two pathways.[762–764] An early example is that regarding the alkylation of lithium anthracene with optically active 2-octyl halides and mesylate (Scheme 46).[764] The observation of partial configuration inversion in the product of the monoalkylation process was interpreted as being the result of the involvement of a $S_N2$ process in conjugation with the SET initiation. Further investigations using optically active alkyl halides and the electrochemically generated radical anion of anthracene took

**Scheme 47**



advantage of the important kinetic and thermodynamic data that electrochemical techniques can provide.[765] Products of both the $S_N2$ (inverted product) and the SET-initiated process (racemic product) were identified and quantified. Based on the relative yields, the competition between the two processes has been shown to favor the SET-initiated process for the 2-octyl halides. The electrochemical generation of radical anions played an important role in excluding the possibility of an inversion as a result of a reaction with the anthracene dianion.[765] This dianion is obtained through disproportionation of the corresponding radical anion, and is inhibited under electrochemical conditions where a constant potential is applied.

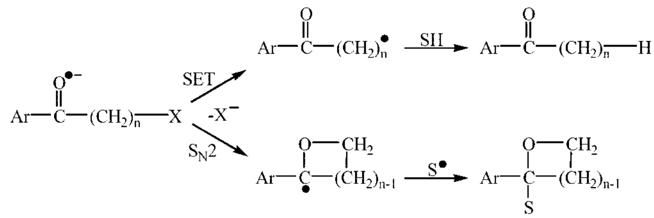
Stereochemical analysis has also been used to show that sterically hindered alkyl halides, such as bornyl and norbornyl bromides, undergo exclusively reduction and not $S_N2$ substitutions when reacted with anthracene radical anion.[767]

Interestingly, the two mechanisms (SET and $S_N2$) have been shown to coexist, at variable activation enthalpies, in the reaction of butyl bromides with the electrochemically generated anthracene radical anion.[768] The Arrhenius plot for the reaction with *n*-butyl bromide showed two linear regions, where the slope is larger at relatively higher temperatures. This has been interpreted as an indication of a transition from a SET to a $S_N2$ process on decreasing the temperature.

Another interesting example is that illustrated by the reaction of the electrochemically generated 1,4-dicyanonaphthalene radical anion with a series of substituted benzyl bromides in DMF.[769] The study also showed that both mechanisms are occurring (Scheme 47) and that a transition from a preferred SET to dominant $S_N2$ process depends on the nature of the ring substituent. Such a transition was not observed in acetonitrile, and it has been suggested that the transition is a consequence of the effect of the solvent on the $S_N2$ transition state.

The electrochemical reductive alkylation of iron in porphyrin complexes using alkyl halides is worthy of attention.[770] The reaction of the electrochemically-generated iron(I) (and even iron(II) at higher alkyl halide concentrations) in porphyrins with *n*-alkyl halides has been shown to lead to $\sigma$-alkyl iron porphyrins through a mechanism that has clearly been shown to involve a $S_N2$ process. Kinetic analysis of the reaction showed that the rate constant depends on the nature of the halogen in the alkyl halide, the reaction being faster in the order I > Br > Cl, and on the electron donating ability of the porphyrin ring. The experimental rate constants were much larger than expected for an outer-sphere ET between the iron(I), in the porphyrin, and the *n*-alkyl halide. Further insights have been gained by studying the reaction of iron(0) porphyrins with alkyl halides. The greater reactivity of iron(0) allowed extension of the study to secondary and tertiary alkyl halides.[768,771] The $S_N2$ character of the reaction was thus confirmed through a number of studies.[768] Larger rate constants were found for the reaction of *n*-butyl bromide with unencumbered porphyrins (either iron(0) or iron(I)) compared to a radical anion with a similar standard potential. Considering the same porphyrin, the reaction rate constant decreased going from *n*- to *s*-, to *t*-butyl bromide. For the same alkyl halide, steric hindrance at the metal center of the porphyrin caused a similar effect.

**Scheme 48**



The role of the leaving group in influencing the SET/$S_N2$ dichotomy has also been investigated in the reaction of the anthracene radical anion with methyl halides. While the $S_N2$ process is favored for methyl chloride, it decreases in favor of SET initiation for methyl bromide, and even more for methyl iodide.[772]

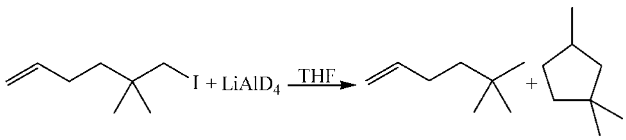
The advantage of using pulse radiolysis to study the $S_N2$/SET dichotomy is its ability to provide kinetic data and in identifying reactive intermediates.[773–775] A relevant example is the competition between an intramolecular SET and a $S_N2$ pathway that has been reported for the reaction of substituted 1-benzoyl-$\omega$-haloalkane radical anions.[774,775] The pulse radiolysis generated radical anions led to intramolecular SET and nucleophilic substitution products through further reaction with the solvent (Scheme 48). The reaction rate constants, and hence the competition between the two mechanisms, were shown to depend on the nature of the halide leaving anion. The $S_N2$ process was shown to be more efficient following the order I > Br > Cl. The polarity of the solvent has also been found to affect the reaction rates.[775] Another factor found to affect the rate constant of the decay of the radical anion was the reduction potential of the corresponding acetophenone, which is monitored through introduction of a variety of substituents. The ET pathway was found to be more predominant for rapidly decaying radical anions. The importance of the spatial configuration of the systems investigated and its consequence on the geometry of the transition state involved were also briefly discussed.[774]

The extent of the involvement of SET process in traditionally accepted $S_N2$ processes was also investigated using homogeneous catalysis. ET rate constants for reactions of alkyl halides and a series of electrochemically-generated donors were determined and the corresponding activation−driving plots constructed. These plots were used to estimate ET rate constants for the reaction of the radical anions with a specific substrate. The potential involvement and extent of a SET process were probed through comparison of these estimated ET rate constants with the experimental ones. An example is the reaction of the 1,4-dihydromethoxycarbonyl-1-methylpyridine anion with a series of sterically hindered alkyl bromides including *t*-butyl, neopentyl and adamantyl bromides. The occurrence of an initial SET step in the route to the substitution products was shown.[251] A similar investigation involving the reaction of the same anion, as well as a series of electrochemically generated radical anions, with alkyl halides confirmed both SET and polar pathways. The substitution yield increased with increasing steric hindrance while the benzyl halides only produced the corresponding reduction products.[776]

**Scheme 49**

$$RX + LiAlH_4 \longrightarrow RH + LiX + AlH_3$$

**Scheme 50**



It was concluded that, for a large variety of nucleophiles (and to a lesser extent radical anions), the $S_N2$ process is faster than the SET for reactants that are not sterically hindered.[251,266,771,776–779]

An even more accurate approach consisted of comparing the experimental rate constant with that obtained through application of the DET theory. It provided further support for these conclusions and allowed better a rationalization of the results observed. Thus the difference between experimental and predicted rate constants has been clearly shown to depend on steric hindrance. The values are in agreement for sterically hindered reactants, indicating the predominance of the SET pathway.[468] Studies on the effect of the temperature on the nucleophilic substitution kinetics for such systems showed an increase in the entropy of activation as the steric hindrance increases.[768,780,781] These results agree with previous conclusions for nonhindered reactants, since the experimental values are found to be larger than the estimated ones. This indicates that the $S_N2$ pathway is favored.[468]

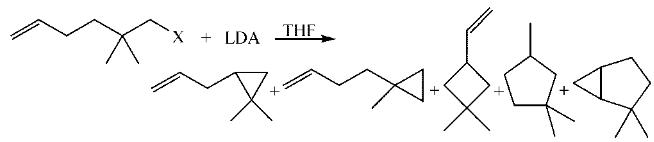
There is some controversy with regard to the reactions of many other nucleophiles with various substrates including alkyl halides; although SET initiation steps have been suggested, this has been challenged in many cases and other mechanisms have been proposed. In some studies, the involvement of an initial SET was ascertained based on the experimental detection of radial intermediates using techniques such as ESR and CIDNP, or through the use of either radical traps or cyclizable radical probes. These include nucleophiles such as metal alkyls,[782] metal hydrides,[783–793] alkoxides,[794–796] enolates,[797–800] trimethyltin anion,[801–803] dialkyamides,[804–810] alkalistannanes,[801–803,811,812] organocopper species[813] and diisopropylamide.[814] One controversial example is that concerning the well-known[815–822] reduction of alkyl halides using lithium aluminium hydride, $LiAlH_4$ (Scheme 49). In this particular example, the potential involvement of an ET versus a purely polar process stimulated an interesting debate.

On the one hand, it was suggested that the reduction involved a SET initial step for alkyl iodides. This was based mainly on radical trapping and cyclizable radical probe results.[788,823–825] A similar mechanism was suggested for $LiEt_3BH$ and $LiH_3$.[818–822,826–830] The initial argument in favor of an ET process, involving a radical intermediate, was based on the reduction, using $LiAlD_4$, of cyclizable alkyl iodides such as 6-iodo-5,5-dimethyl-1-hexene, as shown in Scheme 50 leading to mixtures of deuterated and nondeuterated products.

The formation of both straight chain and cyclic nondeuterated products was believed to be the result of abstraction by a radical intermediate of a solvent hydrogen atom.

On the other hand, based on kinetic analysis and radical probe studies this was challenged. Results implied that the initial SET may not in fact be an important pathway in these reactions.[791,792,831–834] Studies suggested that alkyl halide probes may not be a reliable probe for ascertaining either the occurrence or the extent of a SET step. One reason is that, like other radical probe alkyl halides, 5-hexenyl iodides are prone to radical chain isomerization to yield the corresponding cyclopentylmethyl iodides.[793] Rearranged products are therefore obtained through a radical process that is not necessarily the reaction of interest.

**Scheme 51**



More in-depth analysis should be undertaken to ensure that the suggested pathways are in fact kinetically possible.[791–793] This controversy had a positive impact since it led to further studies based on the custom design of structurally interesting alkyl halides aimed at either favoring or disfavoring specific steps of the overall process,[791,793,825] although the extent to which one mechanism predominates over the other was not always unambiguously ascertained.

Another interesting example where a hydride anion is transferred both in an ET[814] and a polar[815,835–841]initial step is that for the reaction of lithium dialkyl amides (LADs) with alkyl halides. Here again 6-halo-5,5-dimethyl-1-hexenes were of particular interest and their reaction with LDA led to a variety of cyclic products (Scheme 51).

Three competing pathways were proposed to explain these results: a SET initial step, a carbene forming reaction, and a polar mechanism involving an anionic intermediate.[814]

Trapping SET intermediates in nucleophilic substitution reactions has also been used to investigate the dichotomy between the two processes, especially in the cases where the leaving group and nucleophile are the same (identity reaction).[842] Evidence for an ET process was made for the reaction of 9-mesitylfluorenyl anion with methyl iodide which leads to 9-methylmesitylfluorene. This conclusion was reached through the direct observation of the 9-mesitylfluorenyl radical while monitoring the reaction using UV−vis spectroscopy.[779] Considering the large driving force associated with this reaction, the SET is believed to be "inner-sphere" in nature, with the ET taking place at a near bonding distance between the reacting anion and alkyl halide. Similar conclusions were reached for other examples.[562] This inner-sphere vs outer-sphere debate regarding the SET/$S_N2$ dichotomy has attracted considerable attention.

In addition to the large body of experimental evidence for the involvement of SET in many nucleophilic substitution reactions, interest has also been directed toward theoretical studies. These make it possible to gain a more fundamental understanding of the two pathways as well as the factors controlling them. Two main schools of thought have emerged from the experimental studies. The first considers the two processes as two different competing pathways each going through a distinct transition state on the potential energy hypersurface leading to the substitution product.[468,628,765,768] The second view considers the two pathways as extremes of a single "continuous mechanistic spectrum" with a single transition state.[251,777,843,844]

## 7.2. Theoretical Studies: Bound/Unbound Electron Transfer Transition State?

Due to the importance of both nucleophilic substitution reactions and ET-initiated reactions and because of the controversy that evolved with regard to many of the experimental studies, a more fundamental understanding of the $S_N2$/SET dichotomy appeared necessary. The studies undertaken to investigate the different aspects related included the mechanistic distinction between the two reaction pathways, the factors favoring one process over the other, and the nature of the transition state or states involved.

In some early studies, the treatment of the mechanism of nucleophile reactions with radical cations through SET or polar nucleophilic reactions using the Dewar−Zimmerman rules[845,846] has been both supported[847,848] and challenged.[849,850] It was also suggested, that based on the curve-crossing model,[851−856] polar pathways are more closely related to SET than previously since they involve the shift of a single electron.[843,851−853,857−859] Electron shift has been used to describe electron movement that is coupled with bonding changes in a synchronization and differs from ET processes where bonding changes take place only in subsequent steps. The degree to which even SET transition states are bound or unbound (or in other words outer-sphere versus inner-sphere ET) between nucelophiles and substrates has attracted increasing attention. Based on investigations using the valence bond curve-crossing model, the ET from radical anions to neutral substrates has been suggested as taking place through a bound transition state.[860]

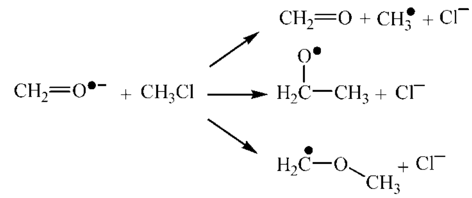
The model used to study the $S_N2$/SET dichotomy between the two mechanisms and the factors controlling it[843,851] has been identified as being crucial to fundamental understanding of the process. Many important parameters have been identified as playing a role: these include the avoidance of crossing interactions, orientation of the reactants, structural distortions in the transition states and subsequent solvent reorganization, in addition to the vertical ET energy gap, which is a function of the ionization potential of the nucleophile/donor and the electron affinity of the substrate/acceptor, and delocalization and steric effects of the charge transfer state.[859]

Ab initio quantum chemical calculations of some simple systems provided further insights into the $S_N2$/SET dichotomy despite the fact that different conclusions were reached depending on the wave function (ROHF vs UHF) employed and the coordinate system used to follow the reaction paths. The differences concerned the nature of the main pathway leading to the ET product and the associated transition state. On the one hand, the ET product was found to result from a pathway involving a bound transition state that is common to the polar pathway, which leads to the substitution product. On the other hand, the main pathway leading to the ET product has been shown to involve an unbound outer-sphere ET transition state.

### *7.2.1. Bound ET Transition State*

Initial computational investigations by Sastry and Shaik were for the reaction of the formaldehyde radical anion ($CH_2{=}O^{\bullet-}$) with methyl chloride ($CH_3Cl$).[861,862] The reaction is known to experimentally follow three possible pathways including an ET, a C-alkylation and an O-alkylation as shown in Scheme 52. However, only two transition states were obtained and these were assigned to the ET-dissociative

**Scheme 52**



and the $S_N2$ mechanisms. Intrinsic reaction coordinate (IRC) path following[863] was used to assign the transition states to the reaction pathways.

Figure 24 shows the computed pathways and the key structures for the reaction of the formaldehyde radical anion and methyl chloride. The ET product cluster ($C_{ET}$) is obtained from an initial reactant cluster ($C_R$) and goes through the ET-transition state (ET-TS). That of the O-alkylation product ($C_{SUB(O)}$) is obtained through the substitution transition state (SUB(O)-TS) starting from the same reactant cluster ($C_R$). In the transition state assigned to the ET process, ET-TS, and besides an important reorganization from the O−C−Cl orientation at the reactant cluster, $C_R$, to a C−C−Cl orientation, the C−C bond distance decreases dramatically by about 0.744 Å (from 3.316 to 2.572 Å). Thus indicates a bound transition state with a definitive structure. The entropy associated with the formation of this transition state is comparable to that corresponding to the formation of the ET-SUB(O) transition state. No direct pathway was found for the formation of the C-alkylation product ($P_{ET-SUB}$). The study showed that the only way to this product is by an addition reaction between the methyl radical and formaldehyde, starting from the ET cluster ($C_{ET}$), and going through another transition state ($C_{AT}$-TS) (Figure 25). Accordingly, C-alkylation was viewed as a two-step process involving an initial SET followed by addition of the methyl radical to the formaldehyde. O-alkylation is possible through a similar process but involves a transition state which is much higher in energy. It was, however, mentioned[862] that outer-sphere (weakly interacting or unbound) ET transition states may be found. Subsequent studies from this and other groups were particularly concerned with the nature of these transition states.

The reaction of formaldehyde with methyl chloride, $H(CN)CO^{\bullet-}$ with methyl chloride and that of $\omega$-chloroalkanal radical anions ($Cl(CH_2)_nC(H)O^{\bullet-}$, n = 2, 3) were all investigated.[864] Reactions paths were followed at the UHF/6-31G* and ROHF/6-31G* levels in both Z-matrix internal coordinates without (Z-Int) and with mass weighting (MW). Furthermore, the two dimensional potential energy surface provided further insights into the $H_2C{=}CO^{\bullet-}/CH_3Cl$ case. While the Z-Int path was found to lead to the ET products at both calculation levels (UHF and ROHF), substantial differences were found for the MW paths. These were found to still lead to the ET product at the ROHF level but to the C-substitution products at the UHF level. In the latter case, the MW path was actually found to also branch toward the ET products. This was evident from the two dimensional potential energy surfaces as seen in Figure 26, which shows the critical areas.

Both surfaces have two valleys, separated by a ridge: one leads to the ET products and the other to the C-substitution products. The Z-Int paths on both surfaces undergo a downhill descent in the ET valley to the saddle region. This is concomitant with an elongation of the C−C bond, and then continues toward the ET products. The MW path on

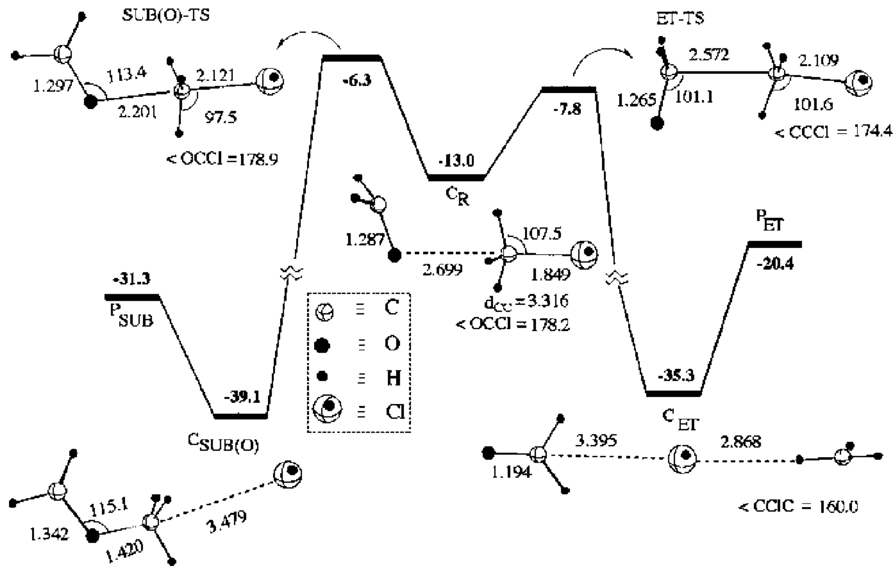



**Figure 24.** UCCSD(T)/6-31+G*//ROHF/6-31G* energy profile for the ET and SUB(O) mechanisms. Profiles are verified by IRC techniques using both IRC-MW and IRC (Z-Int) coordinates. Energies are given in kcal/mol relative to the reactants. Reprinted with permission from ref 862. Copyright 1996 American Chemical Society.

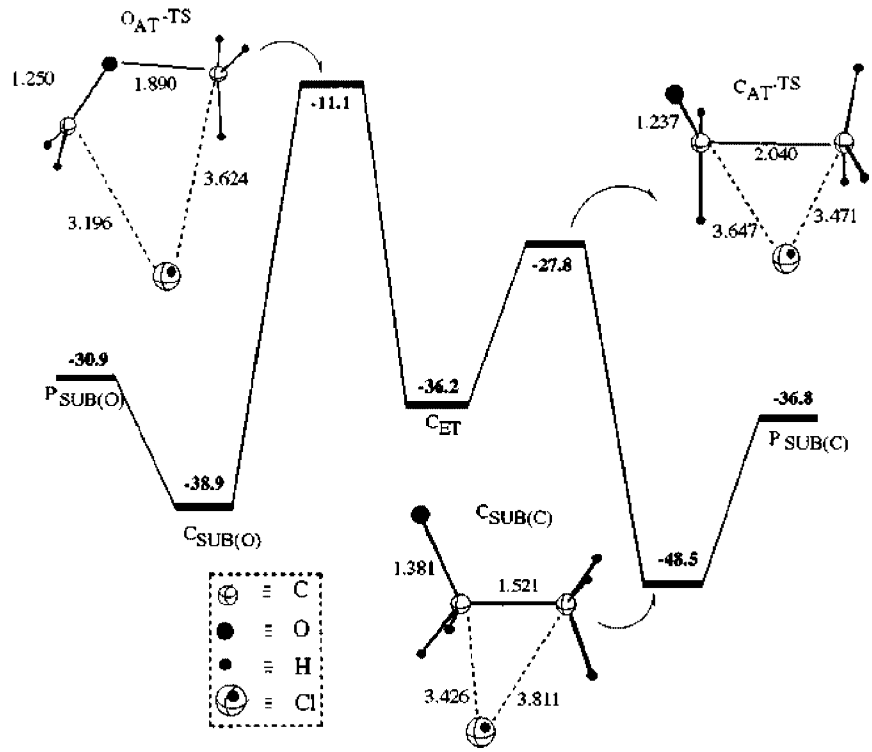



**Figure 25.** UCCSD(T)/6-31+G*//UMP2/6-31+G* energy profile for the $CH_3$ radical attack processes starting within the ET cluster, $C_{ET}$. The energies are in kcal/mol relative to the reactants. Reprinted with permission from ref 862. Copyright 1996 American Chemical Society.

the UHF surface crosses the ridge, with a substantial decrease of the C−C and an increase of the C−Cl bond distances, to the saddle region. Finally it proceeds toward the C-substitution products. The MW path first proceeds in a fashion similar to the ROHF surface but toward the shorter C−C and C−Cl distance area of the saddle region and then proceeds back toward the ET valley to produce the ET products.

In a further study, branching ratios were calculated using ab initio classical trajectories (trajectory calculations) on the Born−Oppenheimer surface for the reaction of formaldehyde and cyanoformaldehyde radical anions with methyl halides.[865] It was found that transition states with shorter C−C distances favor the C-substitution products while those with longer distances favor the ET products. This molecular dynamic study concluded that, although the ET product can be generated from an outer-sphere transition state, it can also form from a strongly bound transition state.

The branching ratios were also investigated as a function of the temperature for the reaction of the formaldehyde radical anion with methyl chloride.[866] The ratio of the ET/C-substitution products increased from 1.02 to 1.43 when the temperature was varied from 148 to 598 K. The temperature dependence of the product ratios was interpreted as resulting from the shape of the potential energy surface

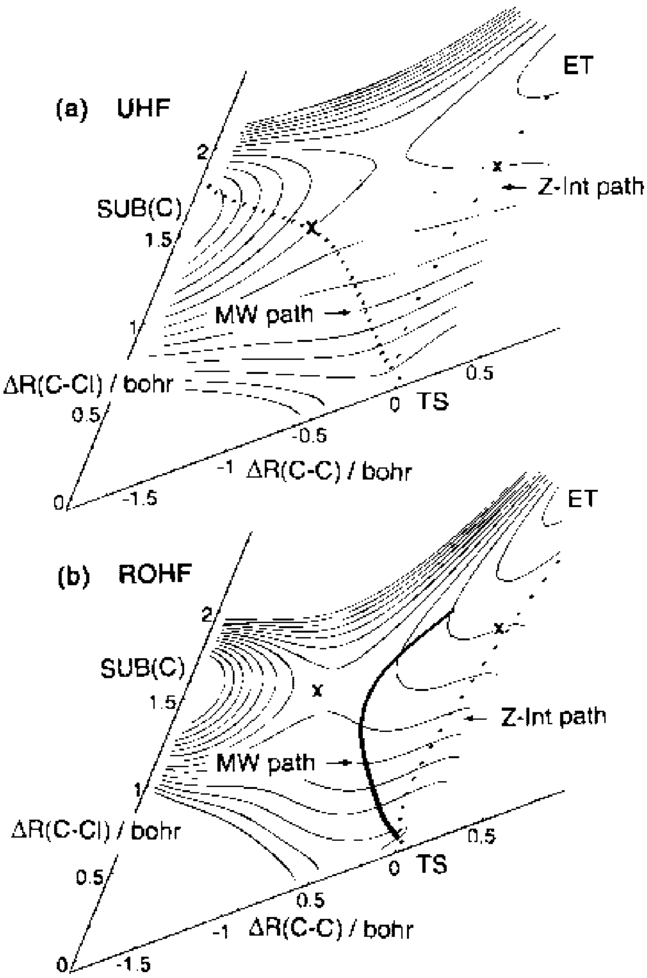



**Figure 26.** Contour plot of a portion of the mass-weighted potential energy surface containing the Z-Int and MW paths for the reaction of $H_2CO^{\bullet-}$ with $CH_3-Cl$ computed at the (a) UHF and (b) ROHF levels of theory (contour lines at 5 kcal/mol intervals). Reprinted with permission from ref 864. Copyright 1997 American Chemical Society.

rather than from the existence of separate transition states for the ET and C-substitution pathways.

For the reaction of cyanoformaldehyde radical anion with methyl, ethyl, isopropyl and *tert*-butyl chlorides, steric hindrance effects on the $S_N2$/ET dichotomy at the level of this bound C−C−Cl transition state have also been probed theoretically.[867] It was found that this transition state leads mainly to the C-substitution products for the less hindered methyl and ethyl chlorides but ET predominates as steric hindrance increases on going to the isopropyl and *tert*-butyl chlorides. The C−C distance in these transition states increases accordingly on going from the methyl to the *tert*-butyl halide.

Ab initio molecular dynamic studies were reported for the reaction of ketyl radical anions with alkyl halides.[868–870] These suggested that the three different mechanisms pass through the bound ($S_N2$-like) transition state. One leads to the formation of the $S_N2$ products, another directly to the ET products and the third involves the formation of ET products but after initial passage through the TS and then crossing over to the ET valley. In the reaction of the formaldehyde radical anion with methyl chloride, higher temperatures were shown to favor direct ET product formation.[869] Dichotomy was found to depend on the electron donating ability of the radical anion (formaldehyde vs cyanoformaldehyde radical anions) as well as on the steric hindrance of the alkyl halide (methyl vs isopropyl chlorides).[870]

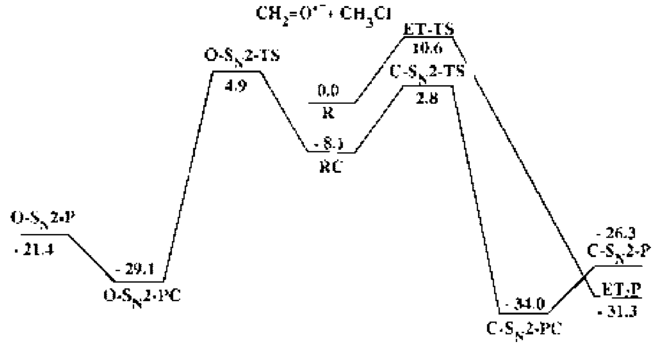



**Figure 27.** Reaction profiles (free energies, MP2 geometries for the reaction of $H_2CO^{\bullet-}$ with $CH_3-Cl$). Reprinted with permission from ref 871. Copyright 1996 American Chemical Society.

### *7.2.2. Unbound Outer-Sphere ET Transition State*

Ab initio quantum chemical investigations of the same reaction (formaldehyde radical anion and methyl chloride)[871] showed the existence of an outer-sphere ET transition state (ET-TS). Two additional transition states (C-$S_N2$-TS and O-$S_N2$-TS) corresponding to the C- and O- substitution reactions, respectively, were also obtained. Figure 27 shows the computed reaction profile and Figure 28 the optimized structures of the key intermediates. The outer-sphere ET-TS is substantially different from those associated with the substitution reactions (C-$S_N2$-TS and O-$S_N2$-TS). In The ET-TS, the two reactants are unbound as they are much more distant from each other and the carbon atom of the formaldehyde radical anion is instead pointing toward to the chlorine atom of the substrate. In the C-$S_N2$-TS and O-$S_N2$-TS, the reactants are much closer together and the carbon and oxygen atoms of the formaldehyde radical anion point to the carbon atom of the methyl chloride (Figure 28).

An interesting result is that more charge transfer from the formaldehyde radical anion to the methyl chloride is observed at the ET-TS (22 %) than at the two substitution transition states (17% and 15% for the O-$S_N2$-TS and C-$S_N2$-TS, respectively). Another important result is that the two substitution transition states in this investigation are very similar to those found in the previous studies in terms of both geometries and energies. The C-$S_N2$-TS is similar to the one described as a bound ET-TS in terms of geometry and energy, albeit with an important difference, and that is the fact that the C-$S_N2$-TS is directly connected to the C-alkylation product cluster and not to the ET product cluster. It is commonly accepted that these discrepancies are the result of the wave function (ROHF vs UHF) employed and the coordinate system used to follow the reaction paths.[864,871]

Similar results were obtained for the reactions of the formaldehyde and ethylene radical anions with methyl fluoride. The ab initio quantum chemical analysis of the formaldehyde radical anion and methyl fluoride reaction provided similar results as for methyl chloride. That is, three similar transition states were obtained. In this instance, the charge transfer at the outer-sphere ET-TS is much larger (96%) compared to only 24% and 36% for the O-$S_N2$ and C-$S_N2$ transition states, respectively. The ethylene radical anion and methyl chloride reaction showed, as expected, two transition states: an outer-sphere ET-TS and a C-$S_N2$-TS.

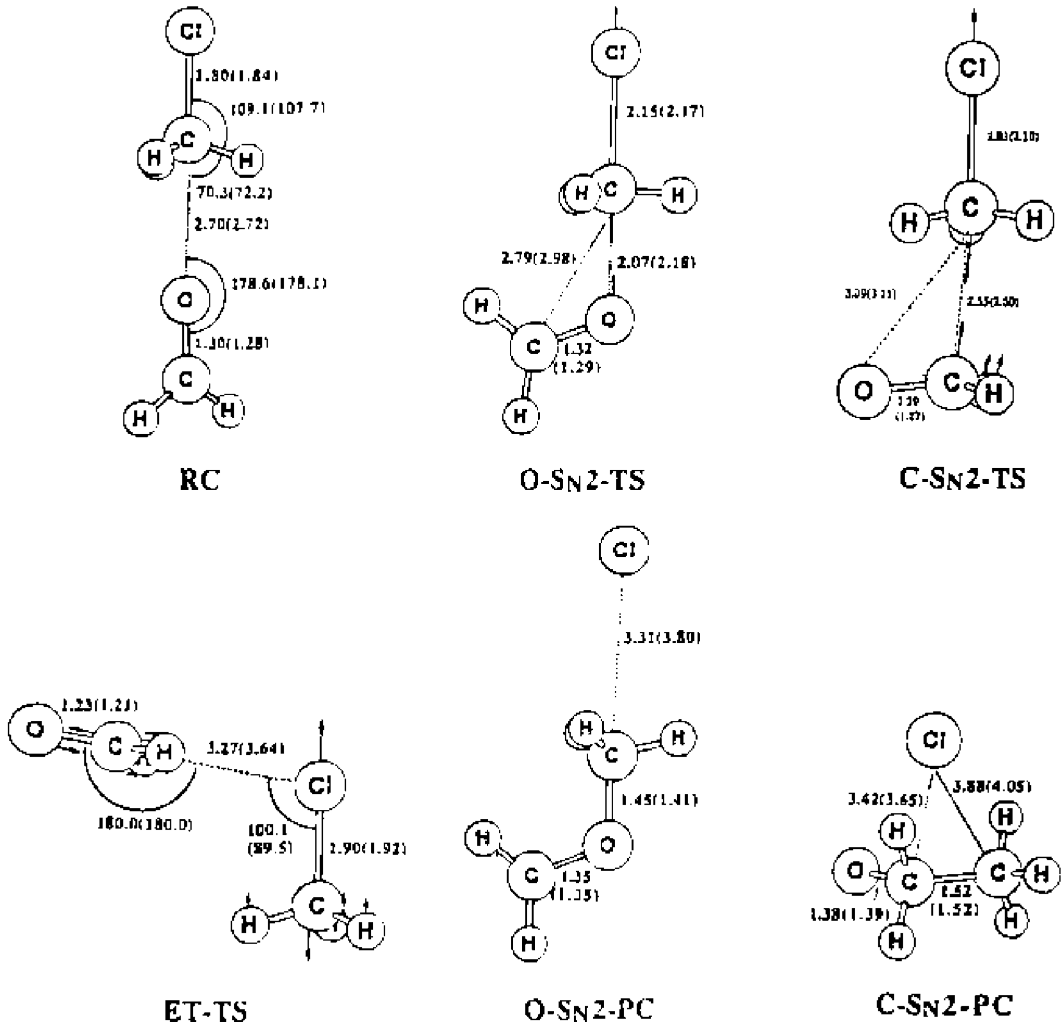



**Figure 28.** Geometries of the minima and transition states in the reaction of $CH_2{=}O^{\bullet -} + CH_3Cl$. Distances are in Å and angles in deg. The numbers correspond to the MP2 and the numbers between parentheses to the HF levels of calculation. Reprinted with permission from ref 871. Copyright 1996 American Chemical Society.

The corresponding charge transfers are 61% and 30%, respectively.

An interesting investigation was the reaction of $NO^-$ with methyl, ethyl, isopropyl, and *tert*-butyl chlorides.[872] Unlike when the formaldehyde radical anion is used, only one substitution is possible in this case and the reaction leads to only two main pathways: the ET and $S_N2$ processes. Here again, in all cases two transition states were observed: one corresponding to the outer-sphere ET, where the nitrogen atom of the electron donor ($NO^-$) approaches the chlorine atom, and the other to the nucleophilic substitution $S_N2$ reaction, where the nitrogen atom of the nuclophile ($NO^-$) instead approaches the carbon bearing the chlorine atom from the opposite side. The outer-sphere ET-TS state is also looser than that corresponding to the $S_N2$ process. This results in a substantial difference between the entropies associated with the formation of the two transition states from the reactant cluster: the vibrational contribution is in the ET process due to the floppiness.

These reactions provided an excellent opportunity for the investigation of the effect of steric hindrance on the $S_N2$/SET dichotomy. The reaction profiles, the key structures and their energies are all shown in Figure 29. One can clearly see how the relative energies of the two transition states are affected as the steric hindrance increases on going from the methyl to ethyl, isopropyl and *tert*-butyl substrates. The energy of the outer-sphere ET-TS decreases concomitantly with an increase of that of the $S_N2$-TS. The ET that is the minor process for the methyl chloride becomes more and more important, eventually becoming the predominant one for the *tert*-butyl chloride.

For the reaction of $NO^-$ with methyl chloride, calculations provided additional interesting insights. The energy of the ET-TS (1.32 eV) was found to be much higher than that of the $S_N2$-TS (0.940 eV). Consequently the formation of the ET product through this TS was predicted not to be important. It was, however, shown that some ET product might be produced through the $S_N2$-TS even if the expected amount to be formed through this indirect pathway is very small compared to the $S_N2$ product. Projection of the reaction paths on the C−N/C−Cl plane provided additional information regarding the effect of steric hindrance on the reaction mechanisms. With the encumbered *tert*-butyl chloride, the ET process predominates over the $S_N2$. Another important result in this report is the bifurcation of the $S_N2$ pathway to also provide the ET product. This is a very important aspect for understanding the fundamentals of the $S_N2$/SET dichotomy.

It is important at this stage to keep in mind that so far only a handful of reactions have been theoretically studied. Extension to other examples will certainly bring more insights.

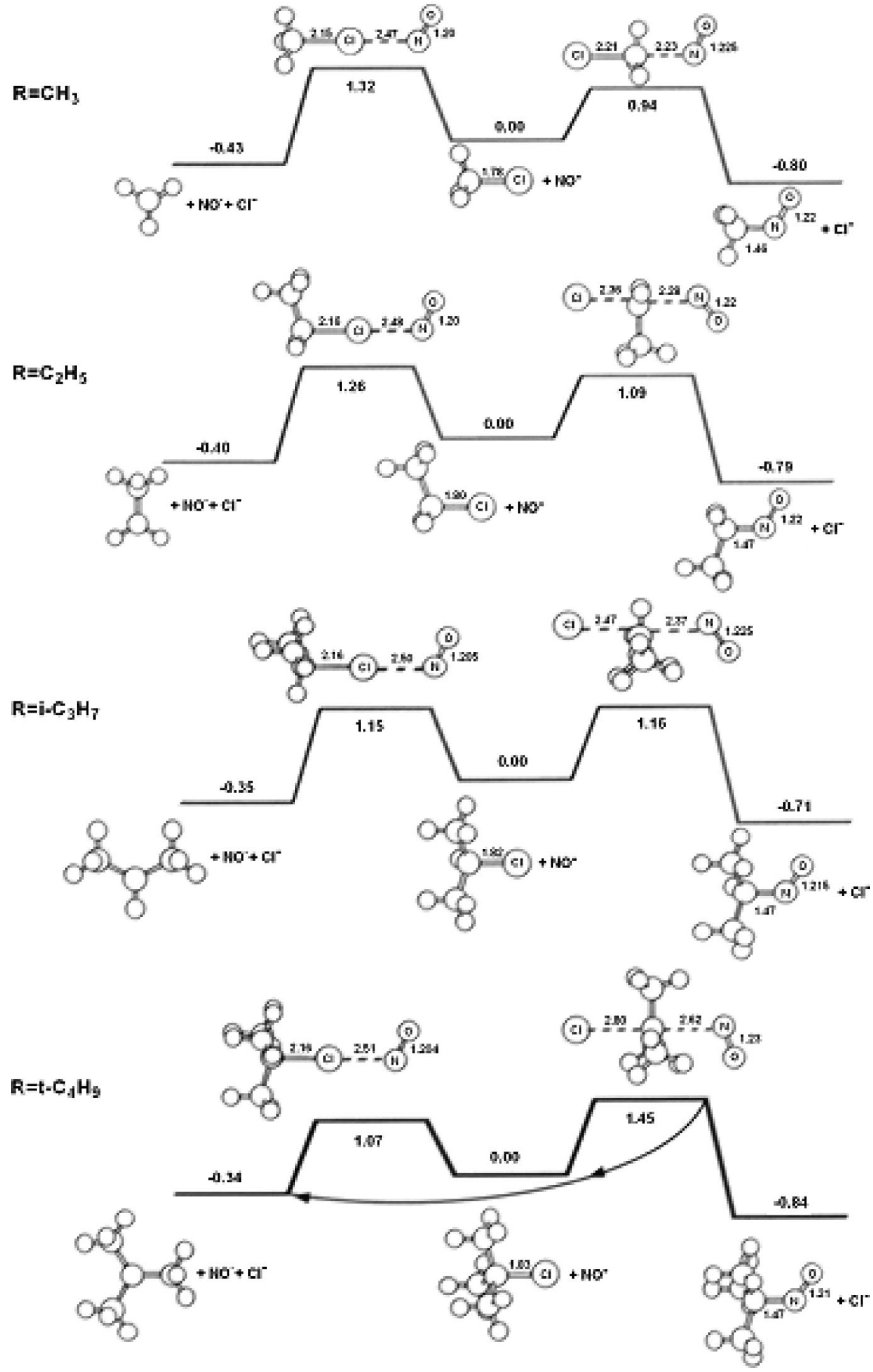


**Figure 29.** Reaction profiles and geometries of the minima and transition states in the reaction of $NO^- + RCl$. Adapted with permission from ref 185 (p 245). Copyright 2006 Wiley & Sons, Inc..

## 8. Concluding Remarks

It is well-known that numerous chemical and biological reactions are triggered by an initial ET. This is related to the fact that the formation of a new chemical bond and/or the dissociation of an existing one can readily be achieved through the oxidation or reduction of an organic or a bioorganic molecule. The field has witnessed a tremendous growth in the last few decades, and the available literature offers extensive examples in this regard. While the importance of ET-initiated reactions from a synthetic standpoint has been long recognized, much effort has also been put into elucidating the mechanistic details of the ET process as well as the concomitant steps.

An important aspect of ET reactions is that the addition or removal of an electron can be triggered by various methods. This particularity has allowed the emergence of a wide range of techniques and methodologies that can be used to investigate different aspects of ET reactions under different conditions. Systematic quantification of the kinetics and thermodynamics has thus been possible using mainly electrochemical and photochemical techniques. This experimental progress has had a real impact on the field since it provided the tools to define the scope and limitations of variable proposed ET models and thus helped the high degree of understanding of ET reactions that exists today. Accordingly, the kinetics, thermodynamics and in-depth details about the mechanisms involved are, in most cases, readily accessible.

"What is the nature of the initial step" is one of the important questions that attracted considerable attention in examining ET-initiated bond making and bond breaking reactions. Two major mechanisms have been identified. The first is the stepwise mechanism, where the ET induces only some reorganization of the organic molecule and leads generally to an intermediate. This process is generally associated with a relatively low intrinsic energy barrier since the internal reorganization energy involves only slight variation of certain angles and bond lengths within the structure. Cases have been reported, however, where more important reorganization takes place leading to a considerable increase in the reorganization energy and hence of the intrinsic barrier. The second mechanism is the concerted process, which is associated with many dissociative ET reactions. Here the ET and the bond cleavage are simultaneous. The concerted mechanism is associated with a large intrinsic barrier since it includes, in addition to the external reorganization, a contribution from the dissociated bond. From a thermodynamic standpoint, the simultaneity of the ET and bond cleavage offers the overall process a higher driving force compared to the stepwise mechanism.

The factors controlling this first ET and the potential occurrence of a transition between the two main mechanisms (stepwise vs concerted) have been well rationalized. Both thermodynamic and kinetic factors are involved in this mechanistic transition. Under favorable conditions this can be induced, through variation of the reaction driving force. In electrochemistry, this has been achieved for ET through variation of the potential, the donor or acceptor, as well as the solvent and the temperature. Even if, under electrochemical conditions, the mechanistic investigation of ET reactions has, in most cases, been straightforward, it is only recently that greater insights have been gained for photochemically initiated dissociative ET reactions. An important aspect is the ability to assign the ET mechanism involved. Under photochemical conditions, this has been based traditionally on quantum yield determination when no intermediate is detected. Recent experimental and theoretical work has shown that this is not an adequate way for discriminating between the two main mechanisms. Hence, the expectation of a quantum yield close to unity for a concerted process is a misleading one.

It has been shown that both mechanisms can be associated with interesting behaviors affecting the dynamics of the ET reaction. On the one hand, the intermediate generated through a stepwise mechanism can in certain cases involve substantial reorganization. On the other hand, the fragments generated through a concerted mechanism can efficiently interact within the solvent cage. In both cases, the intrinsic barrier is higher than that for a stepwise mechanism but smaller than that corresponding to a concerted process. In the second case, the dissociative ET model has been successfully extended to take into account the presence of such interactions between the fragments produced. These in-cage interactions can be confirmed and quantified through comparison of experimental kinetic and thermodynamic data with that predicted using the "sticky" dissociative ET model. It is worth nothing that these interactions have been also shown to impact on the outcome of the overall reaction even where two competitive processes coexist.

Another important aspect when investigating ET reactions is that subsequent steps leading to the initial ET can also be investigated. A large variety of reactions involving neutral structures, radicals, ions, and radical ions have been analyzed in this way and their dynamics well understood. A particular case is the dissociation of an intermediate generated through an ET and its reverse reaction consisting of the recombination of the fragments. This reaction has been shown to involve either a homogeneous cleavage with no charge transfer or a heterogeneous one involving the transfer of a charge. In the latter case, the dissociative ET theory has been extended. This was achieved through the inclusion of the bond dissociation energy of either a cleaved or recombined chemical bond at the level of the ET intermediate. This is generally weaker than that for the parent molecule before ET.

More recently, interest has been focused on long-range intramolecular dissociative ET reactions. While an increasing number of examples are being found involving the dissociation of a chemical bond as a result of an intramolecular ET, more rigorous work is needed in order to fully understand the fundamentals of these reactions. Factors that play an important role in long-range intramolecular nondissociative ET reactions, such as the distance between the donor and acceptor, the nature of the spacer, its geometry and its chemical and physical properties, are expected to also influence the corresponding dissociative reactions.

The dichotomy between a SET initiation step and an ionic mechanism through nucleophilic attack in a large number of substitution reactions has also been extensively investigated from an experimental standpoint. Despite some controversy regarding specific reactions, it has been shown beyond any doubt that many reactions traditionally believed to follow an exclusive polar mechanism do in fact involve, at least in a competitive manner, a SET initiation. Theoretical investigations have also shed some insight on selected nucleophilic reactions even though these have been shown to depend on the methodology used. This is especially true when it comes to the nature of the involved transition states and the associated reaction profiles. It is certain that further related studies will bring additional insights to this SET/$S_N2$ dichotomy.

Despite the progress made in understanding the formation and dissociation of chemical bonds through ET initiation in organic compounds, many other aspects need to be addressed. For example, there has been much less of a focus on investigating such reactions for inorganic and organometallic compounds. Another concern is that most studies have been done exclusively under reductive conditions. It is important to explore certain aspects of these reactions under oxidative conditions. It is also intriguing that the effect of the solvent has not been addressed thoroughly and that only recently has interest been paid to this interesting aspect. Application to biological systems could bring insights into the dynamics and mechanisms of many important processes such as enzymatic reactions based on ET.

Finally, the potential application of such reactions to other areas needs to be explored. Surface modification and the attachment of electrochemically and photochemically generated intermediates through ET reactions is an attractive alternative to more traditional modification methodologies. Electrochemical modification is of particular interest in this context since, in addition to its ability to generate reactive intermediates in the proximity of the electrode, the presence of an electrical field is believed to help in the orientation of the attached molecules. This should help to overcome problems associated with the presence of defects and lack of uniformity. It is also believed that the local manipulation of surfaces can be achieved through use of a scanning electrode in association with these reactions.

Hopefully this review goes some way toward illustrating the considerable progress made in understanding ET processes in general as well as those associated with the formation or dissociation of chemical bonds in particular. There is no doubt that many of the less explored aspects will be addressed in the future.

## 9. Acknowledgments

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