



# Organic electrosynthesis

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[Année 2022-2023]

# Electrochemistry of organic compounds

## I. Introduction

Electrochemistry is the scientific discipline which studies the exchange of electrons between two species. A chemical compound is oxidised when it loses one or more electrons. In contrast, a chemical compound is reduced when it captures one or more electrons. This electronic exchange between the oxidant and the reductant is called a redox chemical reaction. This reaction could be spontaneous or could require an increment of energy. If the reaction is spontaneous we are in presence of a redox process. If the reaction requires an increment of energy the transformation step involves an electrolysis. An electrolysis is performed by the application of an electric field to two electrodes placed in an electrochemical cell. This typical cell is often constituted by a reservoir of solvent in which the compound to study is dissolved.

Considering an organic compound, the electron transfer can take place either on an heteroatom or on a multiple/single bond.

When the electron transfer takes place on an heteroatom like oxygen, nitrogen or sulfur, the specific redox site could be either the free electronic doublets of the heteroatom in oxidation or the bond connecting the heteroatom to the hydrocarbon skeleton of the organic molecule in reduction. For organic molecules free of heteroatom, the electron transfer occurs on a multiple or sometimes on a single bond either in oxidation or in reduction.

It may be highlighted that an electron transfer on an heteroatom requires less energy than the one taking place on a multiple or single bond. This energetic consideration explains why in a classical solvent such as an aqueous solution some organic compounds without any heteroatom are not oxidable or reduced since the solvent can be oxidised or reduced before the organic compound.

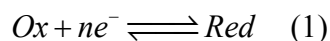
The first part of this report is related to an overview of the different organic functions (yet in a non-exhaustive manner) which are able to be oxidised or reduced.

The second part of the report is based on thermodynamic and kinetic aspects of the electron transfer. These theoretical considerations lead to the answer of the fundamental question: what kind of organic functions are able to be oxidised or reduced?

In which conditions does a specific organic compound can be oxidised or reduced?

## II. Oxidable and reducible organic functions<sup>1,2,3</sup>

As mentioned in the introduction, some organic compounds are able to be oxidised and/or reduced, depending on the nature of the organic functions born by the molecule. In every cases, electroactive organic compounds can be treated as redox couples defined by a standard redox potential  $E_{Ox/Red}^0$ . The relationship between the oxidant and the reductant is called a half electrochemical reaction which can be depicted as follows:



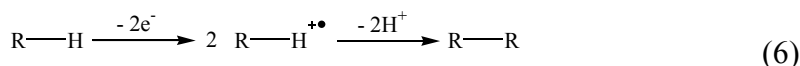
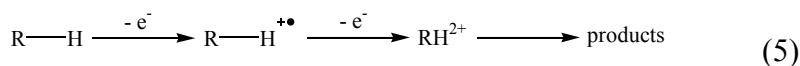
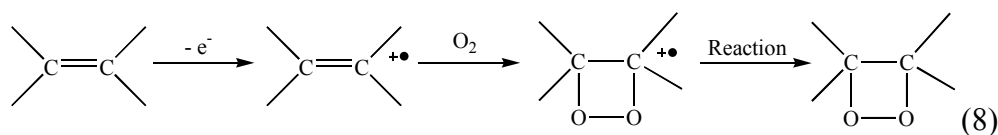
This redox couple leading to a specific standard redox potential  $E_{Ox/Red}^0$  (see section III ) is always reported as:



This chapter is an overview of the electrochemical behaviour of the main organic functions. This paragraph highlights also the fact that the electrochemical behaviour of organic molecules is

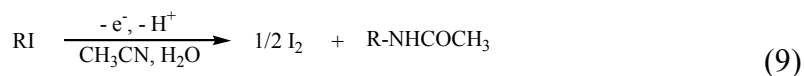
## II.1. Oxidable organic functions<sup>1</sup>

The possibility to oxidise alkanes and alkenes is reported in the literature<sup>1</sup>. In general, such oxidation requires a high potential which could not be reached in aqueous solution (namely higher than 1V/SCE). Nevertheless, equations 3-8 represent the possible electrochemical behaviour of such compounds. More often, the electrochemical oxidation of hydrocarbon compounds leads to neutral radicals. These radicals possess a high reactivity and react with many compounds or trace compounds present in the solution.

$$\begin{array}{c}
 \text{R}-\text{H} \xrightarrow{-\text{e}^-} \text{R}-\text{H}^{\bullet+} \xrightarrow{\text{Nu}^-} \begin{array}{c} \bullet \\ \text{R} \\ \text{H} \end{array} \begin{array}{c} \text{Nu} \\ \text{H} \end{array} \\
 \searrow \\
 \text{B}^- \xrightarrow{\quad} \text{R}^\bullet + \text{BH}^+
 \end{array}
 \quad \begin{array}{l}
 \text{Nu}^-: \text{Nucleophile} \\
 \text{B}^-: \text{Base}
 \end{array}
 \quad (3)$$

$$\begin{array}{c} \diagup \quad \diagdown \\ \text{C} = \text{C} \\ \diagdown \quad \diagup \end{array} \xrightarrow[2\text{Nu}^-]{-2\text{e}^-} \begin{array}{c} \text{Nu} - \text{C} - \text{C} - \text{Nu} \\ | \qquad | \\ \text{---} \quad \text{---} \end{array} \quad (7)$$


### II.1.2. Halogen-containing compounds

The literature<sup>1</sup> is very scarce concerning the electroactivity of halogen containing compounds. The reaction of iodide compounds often leads to the generation of I<sub>2</sub> and to an hydrocarbon species which reacts with the solvent:



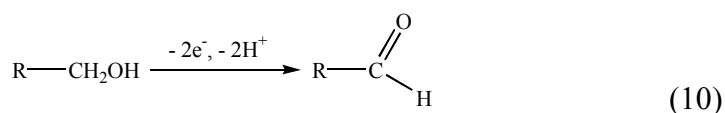
### II.1.3. Oxygen-containing compounds

#### Alcohols:

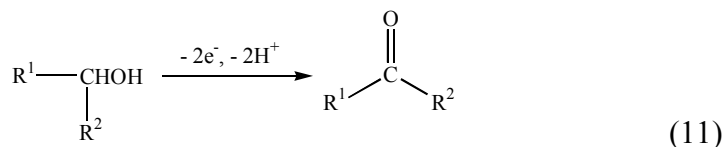
In general, the oxidation of primary alcohols leads to the corresponding aldehyde. The oxidation of secondary alcohols produces ketones, while oxidation of tertiary alcohols gives neutral radicals which are able to be involved in radicalar reactions with the surrounding solvent.

The following equations describe the oxidation of aliphatic alcohols:

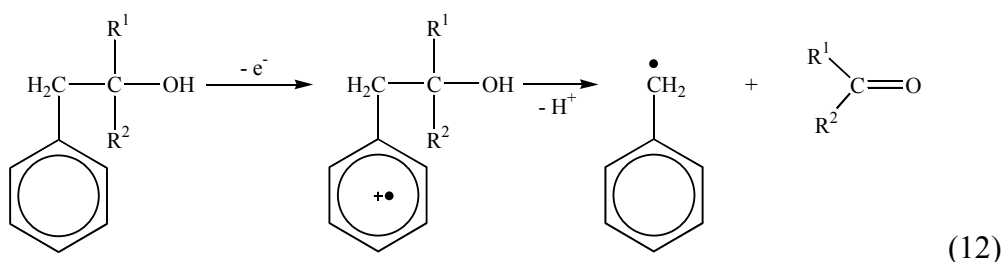
Primary alcohols:



Secondary alcohols :

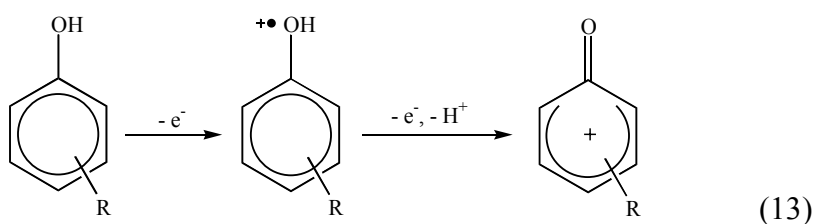


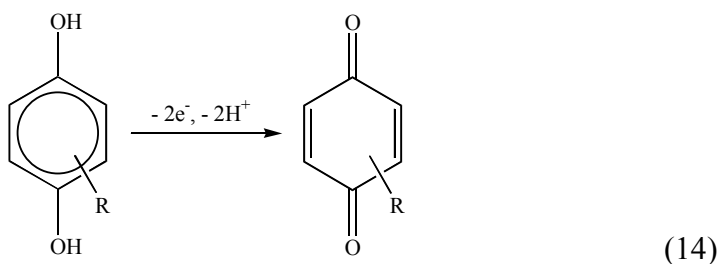
Tertiary alcohols :



#### Phenols and derivatives:

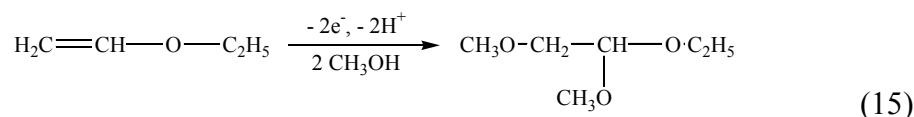
For phenols, the oxidation takes places on the oxygen atom bearing by the aromatic ring and could be described as it follows:





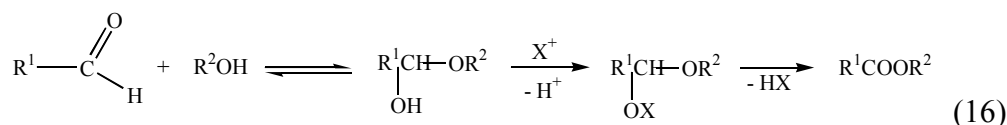
### Etheroxydes:

The predominant reaction of aliphatic ethers during anodic oxidation is the substitution at the  $\alpha$  position from the oxygen atom by a nucleophile solvent. It leads to hydroxy substitution if the electrochemical oxidation is performed in aqueous solution, methoxylation if the electrochemical oxidation is performed in methanol. If the etheroxide function is linked to a small ring, this oxidation leads to a cleavage. The electrochemical oxidation of cyclic ethers takes place by a substitution at the  $\alpha$  position from the oxygen atom by the nucleophilic solvent used to perform the electrochemical oxidation. In the case of unsaturated ethers, the same reaction occurs followed by the addition of one molecule of solvent on the double bond:



### Aldehydes:

Aldehydes are often oxidised into esters using an indirect electrochemical oxidation. The reaction is realised by the electrochemical generation of a halogen mediator. This mediator is obtained by the oxidation of  $\text{Cl}_2$ ,  $\text{Br}_2$ , leading to  $\text{Cl}^+$  or  $\text{Br}^+$ . In the followed equation the electrochemical mediator is represented by  $\text{X}^+$ :

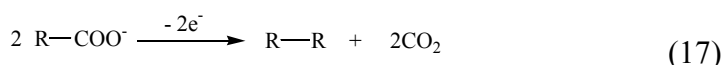


### Ketones:

The oxidation of ketones results in the cleavage of C-C bonds if the ketones contains an  $\alpha$ -alkyl group. This reaction leads to decomposition products.

### Carboxylic acids:

Subjected to an electrooxidation, carboxylic acids tend to produce alkanes through a Kolbe reaction:

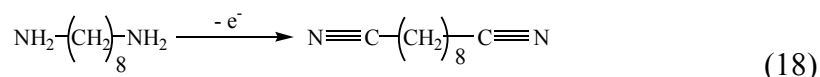


## **II.1.4. Nitrogen compounds**

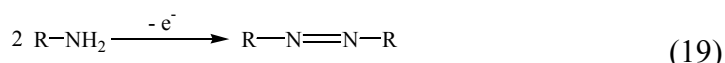
### Primary amines:

Aromatic amines are usually very easy to oxidise. For example, unsubstituted N-alkyl and N,N-dialkyl anilines are oxidised in a potential range of 0.4-1.0 V/NHE (defined in section VI.3.). The anodic oxidation of aromatic amines is quite complex, leading to a variety of products depending on their structure and the electrolysis conditions. In contrast, the anodic oxidation of aliphatic amines leads to simple electrochemical mechanisms.

In general, the oxidation of primary aliphatic amines leads to nitriles when the electrooxidation is performed on a nickel oxide electrode in basic medium:

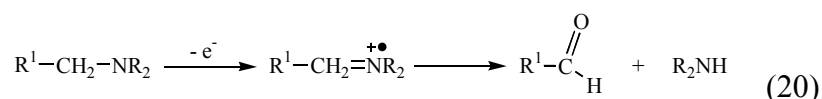


The same oxidation realised on a platinum electrode in tetrahydrofurane leads to diazocompounds:



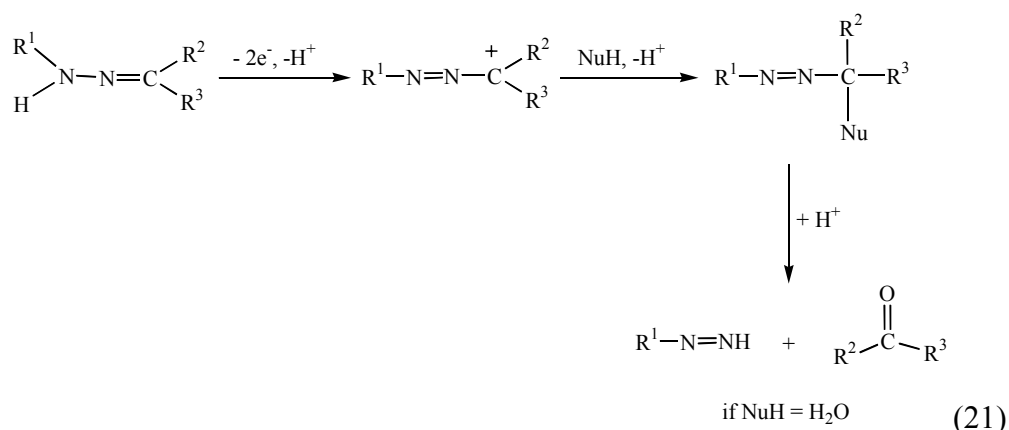
### Secondary and tertiary amines :

The oxidation of secondary and tertiary aliphatic amines leads in acetonitrile to decomposition products such as aldehydes and lower amines :



### Imines:

The anodic oxidation of imines is often followed by the nucleophilic addition of the solvent onto C=N. If the solvent is an aqueous solution, a cleavage occurs:

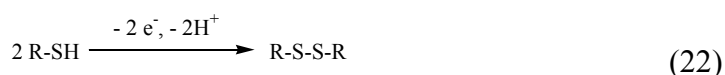


## **II.1.5. Sulfur compounds**

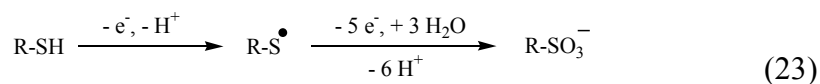
### Thiols:

The oxidation of thiols is strongly dependent on the nature of the medium in which the electrochemical oxidation takes place.

For example, in a non-aqueous medium, the thiols lead to disulfides by electrodimersation:

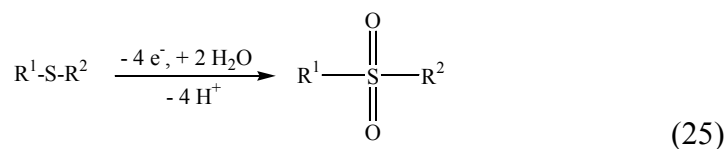
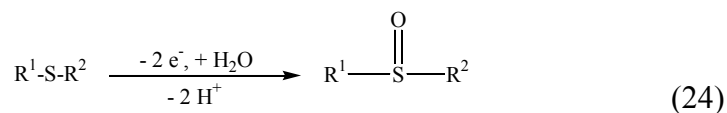


In contrast the oxidation of the same compounds produces sulfonate species in aqueous medium:



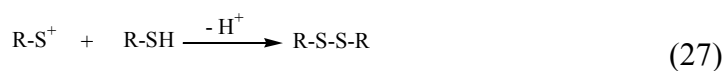
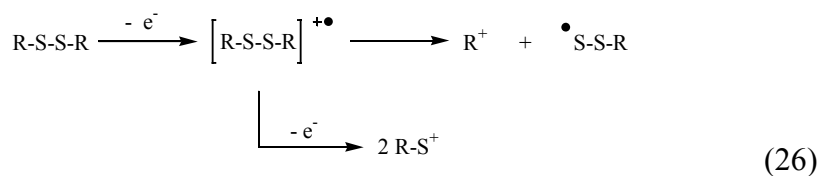
### Thioethers:

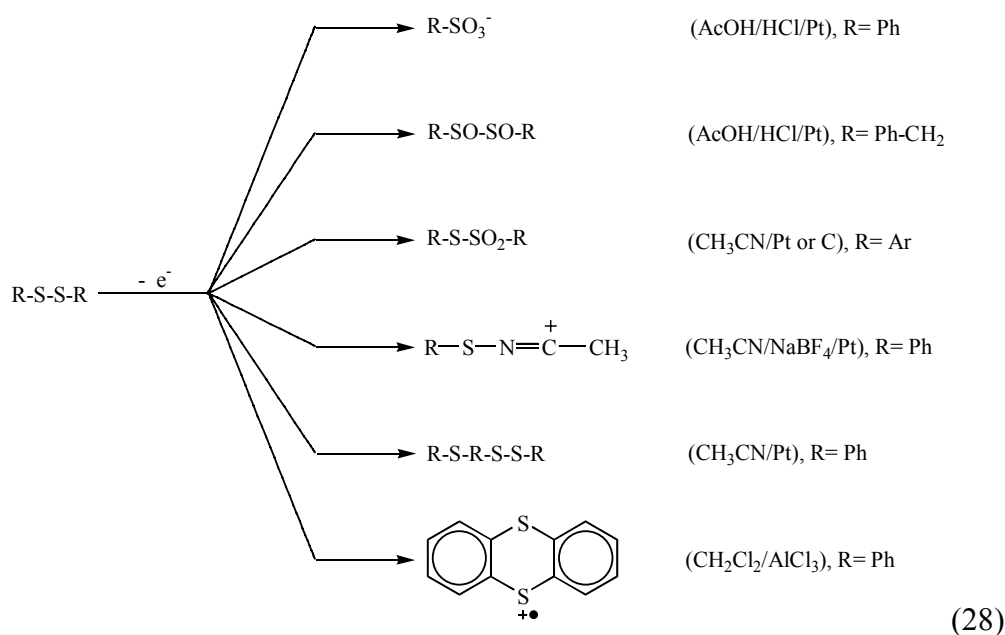
In oxidation, thioethers give sulfoxide by a two electrons process whereas they give sulfones by a four electron process:



Disulfides:

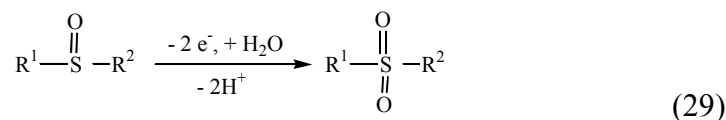
Disulfide compounds are able to be oxidised and lead to various compounds, depending on the nature of the solvent:





### Sulfoxides:

Sulfoxides produce sulfones by a two electrons process:



### II.1.6. Amino-acids :

The electrochemical activity of aminoacids is dependent on the nature of the amino acid side chains. In fact the electrochemistry of such compounds was described below and above. For example, serine and threonine which are primary and secondary alcohols could be treated from an electrochemical point of view directly as alcohols. As another example, tyrosine which bears a phenol group, can be considered as a phenol. Similarly, cysteine could be seen as a thiol.

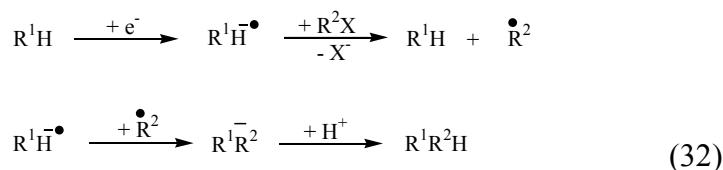
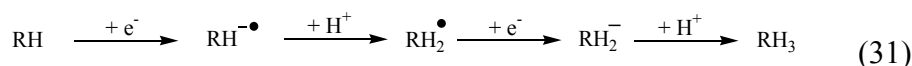
## II.2. Reducible organic functions<sup>1</sup>

### II.2.1. Hydrocarbons

The electrochemical reduction of pure hydrocarbons without functional groups is almost exclusively restricted to unsaturated compounds. The reason is that aliphatic hydrocarbons have extremely low electron affinities that render their reduction impossible.

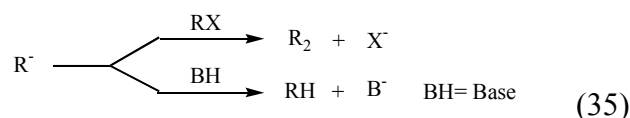
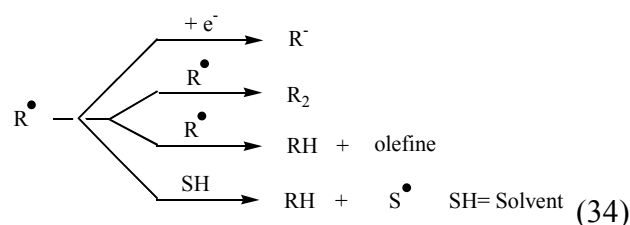
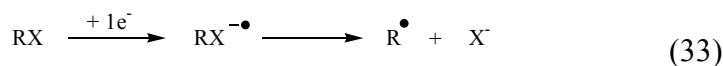


Electrochemical analyses have revealed that the dianion is often instable and reacts with the solvent and with the impurities contained in the solvent. The radical anion which is also quite reactive is able to react with the solvent as well. One can thus observe some protonation, alkylation, acylation, dimerization and polymerisation:



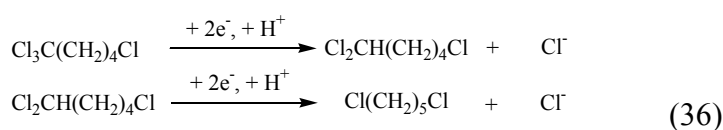
## II.2.2. Halogen-containing compounds

Halogen-containing compounds are able to be reduced producing neutral radicals which are highly reactive:

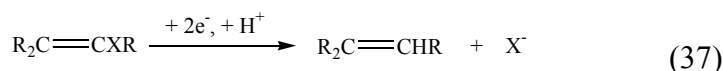


In the type of reaction (35) it can be predicted that RX is able to react with  $\text{B}^-$ , leading to RB or to the an olefine by elimination of  $\text{X}^-$  and BH.

When the reduction takes place on a poly-halogenated organic compound, the electrochemical mechanism could be described as follows:



When the halogen atom is bearing by a double bond, it comes:



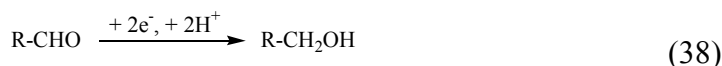
Similar mechanisms are observed for acetylenic compounds.

## II.2.3. Oxygen-containing compounds

Unsaturated oxygen-containing compounds such as aldehydes, ketones, carboxylic acids and derivatives are able to be electrochemically reduced.

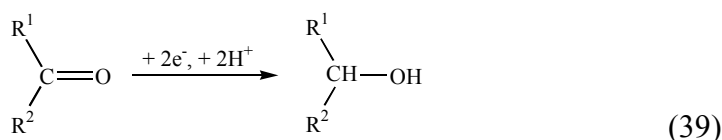
### Aldehydes:

Aldehydes can be reduced in primary alcohols:



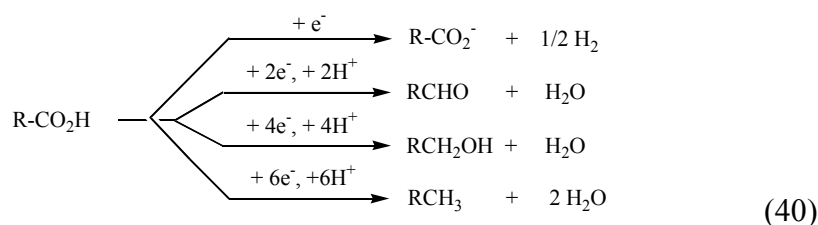
### Ketones:

Ketones are usually reduced into secondary alcohols:



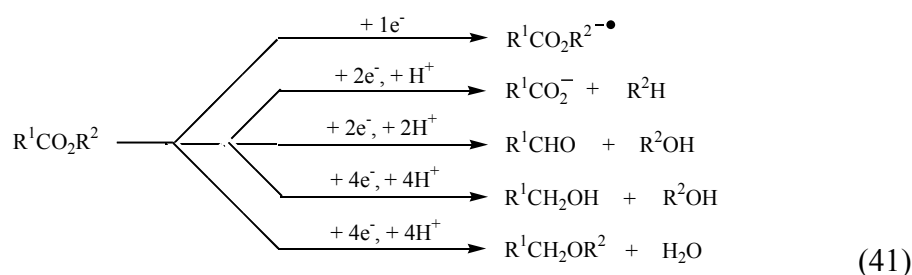
### Carboxylic acids:

The cathodic reduction of carboxylic groups can give the carboxylate anion, the aldehyde, the alcohol or the hydrocarbone in one, two, four or six electron reduction:



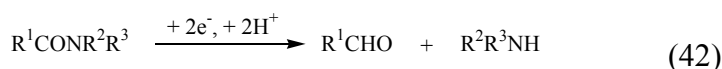
### Esters:

Non-activated esters are reduced with difficulty unless strongly acidic solutions are used. Unsaturated esters such as  $\alpha$ ,  $\beta$ -unsaturated and aromatic esters are reduced relatively easily because of the activating effect of the strongly withdrawing ester group:

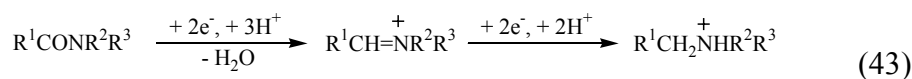


### Amides :

The carbonyl group of amides is reducible leading to the corresponding aldehyde:



In this case the aldehyde can be reduced into the corresponding primary alcohol. Another electrochemical reduction takes place at the same time as the previously described one:

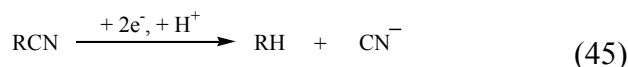
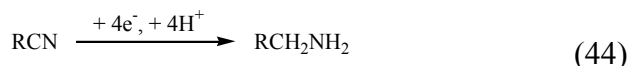


## II.2.4. Nitrogen compounds

Unsaturated nitrogen compounds such as nitriles, nitro or nitroso compounds are reducible:

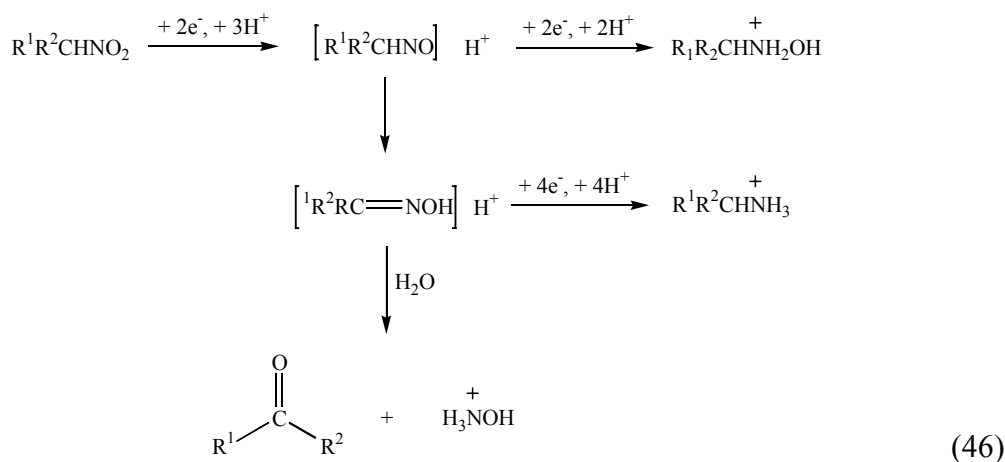
### Nitriles:

Aliphatic and aromatic nitriles are reduced in acidic solution to give amines:

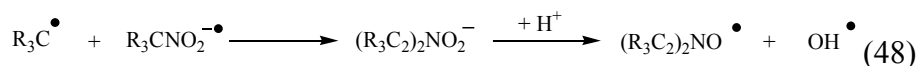
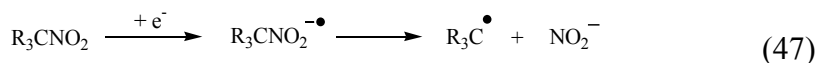


### Nitro compounds

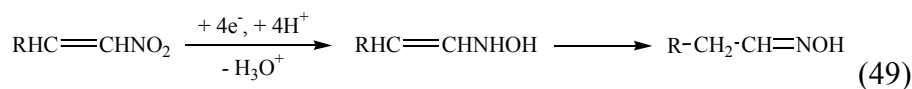
Primary and secondary nitro compounds are reducible in acidic and neutral solutions. Electrolysis of nitro-alkanes in acidic solution at low temperature leads as main product to the corresponding alkylhydroxylamine which is further reducible only in a narrow pH region around pH 7. The mechanism of the reduction can be described as follows:



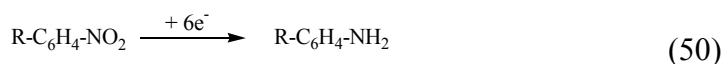
In the case of tertiary nitro-compounds, the intermediate nitroso compound cannot rearrange into an oxime, and this side reaction is avoided. When the reduction is performed in a non-aqueous solvent such as acetonitrile the reduction leads to:



In general, the reduction of unsaturated nitro compounds leads to acetaldoxime which results in a hydroxylamine:

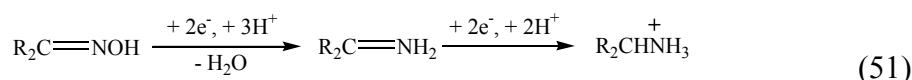


The reduction of aromatic nitro compounds furnishes the corresponding aniline :



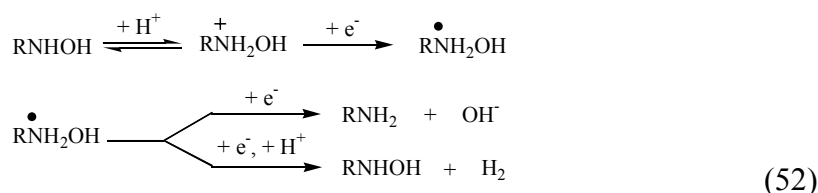
### Nitroso compounds

Primary and secondary nitroso compounds are not stable and tautomerise into oximes. Tertiary nitroso compounds are stable and are generally reduced similarly to the corresponding nitro compounds, leading to an oxime. The reduction of oximes furnishes an ammonium salt:



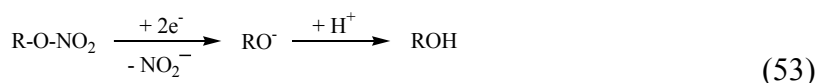
### Hydroxylamines :

Aliphatic hydroxylamines are not easily reduced electrochemically, but a catalysis may occur in acidic conditions:



### Nitric esters:

The reduction of nitric esters leads to the corresponding alcohols:

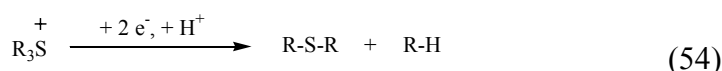


## **II.2.5. Sulfur-containing compounds**

Sulfur-containing compounds are reducible and especially thioethers, disulfides, sulfoxides and sulfones:

### Thioethers:

The reduction of thioether salts produces a thioether and an alkane:



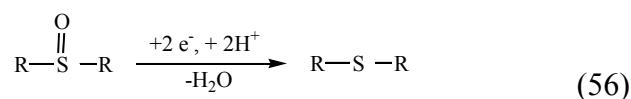
### Disulfides:

Disulfides are able to be reduced into the corresponding thiol:



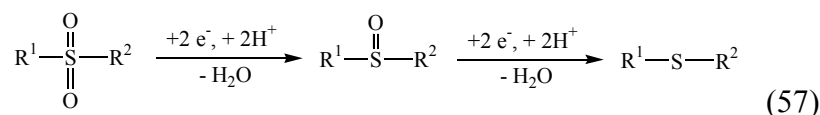
### Sulfoxides:

The reduction of sulfoxide lead to the corresponding thiol:



### Sulfones:

The reduction of sulfone gives sulfoxides and at least thiols:



## **II.2.6. Amino acids**

As it was previously highlighted in the paragraph concerning the oxideable groups, the reactivity of amino acids is rather the same than the one of their side chain.

## **II.3. Summary**

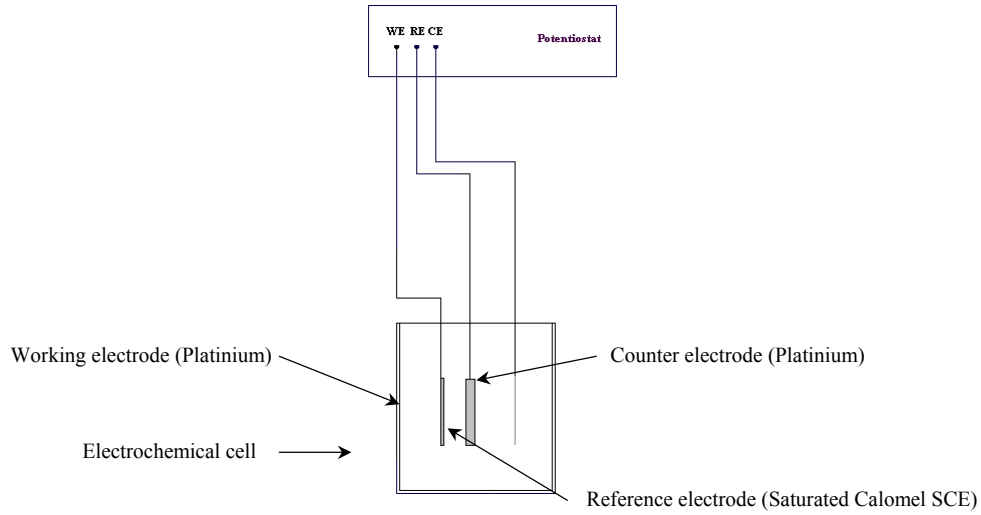
We have described in this chapter main reactions that organic functions subjected to oxidation and/or reduction could underwent. This classical review is not exhaustive and due to the complexity of the involved electrochemical mechanisms and the strong dependence of the electrochemical mechanisms versus the different experimental setups, a specific bibliography is often requires for a specific compound and especially if this one is polyfunctional. For more details concerning electrochemical reactions, once could refer to the bibliographic reference<sup>1</sup>.

## **III. Thermodynamic of the electronic transfer<sup>4,5</sup>**

To access to the thermodynamic parameters of an electrochemical reaction such as the standard redox potential  $E_{\text{Ox/Red}}^0$  of a redox couple, an electrochemical measurement using an classical electrochemical cell is often required. These electrochemical methods allow one also to answer the following question: is the studied organic compound liable to oxidation or reduction.

### **III.1. Electrochemical cell for electrochemical measurements**

A typical electrochemical cell is constituted by three electrodes such as a work electrode (Platinum for example), a counter electrode (Platinum electrode for example) and a reference electrode such as a saturated calomel electrode (SCE). The voltage is applied as a potential difference between the work electrode an the reference electrode. The work electrode is polarised, the reference electrode is not polarised and the counter is polarised as well but no electrochemical reaction occurs at this electrode. This electrochemical technic requires a potentiostat to applied the voltage. A typical electrochemical cell could be described by the following synoptic scheme:



The potentiostat could act either as a source of tension or as source of current.

When no voltage is applied, the potentiostat acts only as a voltmeter only recording the difference of the potential established between the work electrode and the reference electrode. In that case the system is at the thermodynamical equilibrium and the potentiostat record the rest potential  $E_{i=0}$  given by the Nernst equation.

### III.2. Nernst equation of an non polarised system

When we are in presence of a redox couple  $Ox/Red$  with a certain standard potential  $E_{Ox/Red}^0$ , the half electrochemical equation related to this couple is written:



The standard free energy of the system is given by:

$$\Delta G_{Ox/Red}^0 = -nFE_{Ox/Red}^0 \quad (59)$$

At the thermodynamical equilibrium, the mass action law gives the relationship between  $\Delta G^0$  and  $\Delta G$ , the driving force of the electrochemical system:

$$\Delta G = \Delta G^0 + RT \ln \prod_i a_i^{\nu_i} \quad (60)$$

Applied to a redox reaction in witch  $\Delta G = -nFE$  and  $\Delta G = -nFE_{Ox/Red}^0$  it comes the classical Nernst equation:

$$E_{i=0} = E_{Ox/Red}^0 + \frac{RT}{nF} \ln \frac{a(Ox)}{a(Red)} \quad (61)$$

which can be described in terms of the bulk concentrations of the oxidant and the reductant:

$$E_{i=0} = E_{Ox/Red}^{0'} + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]} \quad (62)$$

In this last equation  $E_{i=0}$  is the rest potential,  $E_{Ox/Red}^{0'}$  is the formal redox potential,  $R$  is the rare gas constant ( $8.315 \text{ JK}^{-1}$ ),  $T$  is the temperature in K,  $n$  is the number of exchanged electrons,  $[Ox]$  is the bulk concentration of the oxidant and  $[Red]$ , the bulk concentration of the reductant.

The Formal redox potential is the redox potential that could be access by the experiment. The formal redox potential could be linked to the standard redox potential by the followed relation:

$$E_{Ox/Red}^{0'} = E_{Ox/Red}^0 + \frac{RT}{nF} \ln \frac{\gamma_{Ox}}{\gamma_{Red}} \quad (63)$$

In which  $\gamma_{Ox}$  and  $\gamma_{Red}$  represent the activity coefficient of the oxydant and the reductant respectively.

In many cases, considering very diluted aqueous solution, the activity coefficient  $\gamma \rightarrow 1$  leading to:

$$E_{Ox/Red}^{0'} \simeq E_{Ox/Red}^0 \quad (64)$$

### III.3. Application of the Nernst equation to an electronic transfert :

When no tension is applied to the electrochemical cell, *via* the potentiostat, the thermodynamical equilibrium is represented by the Nernst equation and according to the fact that the formal and the standard redox potential are considered equal, it comes:

$$E_{i=0} = E_{Ox/Red}^0 + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]} \quad (65)$$

When the potentiostat polarise the work electrode to a potential  $E > E_{i=0}$ , the equilibrium is shifted to the production of the oxidant and thus an oxidation is produced.

When the potentiostat polarise the work electrode to a potential  $E < E_{i=0}$ , the equilibrium is shifted to the production of the reductant and thus an reduction is produced.

$$\begin{aligned} E > E_{i=0} &\Rightarrow \text{Oxidation} \\ E < E_{i=0} &\Rightarrow \text{Reduction} \end{aligned} \quad (66)$$

The following curve shows the current response for different applied potentials:

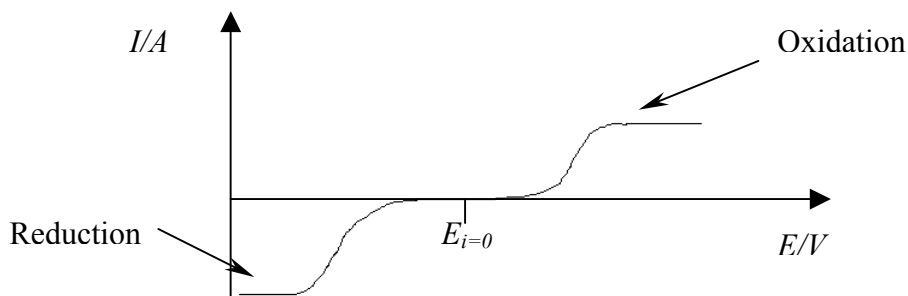


Figure 1: Polarisation curve of an organic specie

## IV. Kinetic of the electronic transfer<sup>4,5</sup>

We have shown that when no tension is applied to the electrodes of the electrochemical cell the electrochemical system is at the thermodynamic equilibrium in which the rest potential  $E_{i=0}$  is given by the Nernst equation. When the electrodes are polarised by a potential  $E > E_{i=0}$  the system evolves through the production of the oxidant whereas when the applied potential  $E < E_{i=0}$  the system evolves through the production of the reductant. In theory this means that a positive difference of potential  $E - E_{i=0}$  leads to an oxidation whereas a negative difference of potential  $E - E_{i=0}$  negative leads to a reduction. This view is correct only for very fast electron transfer, i.e., when no kinetic effect is considered. The kinetics of the electron transfer indeed plays a important role on the effective applied potential required to displace the thermodynamic equilibrium toward an oxidation or a reduction. This required increment of potential is called the overpotential  $\eta$  and describes the kinetic of the electron transfer taking place on a molecule.

### IV.1. The overpotential

If theoretically a slight difference of potential is required to oxidise a product or to reduce it, very often the potential difference that has to be applied to induce the oxidation and/or the reduction is larger than expected. This difference between the theoretical potential and the real potential to apply is called the over potential  $\eta$ .

The oxidative potential to apply to the system is given by:

$$E = E_{i=0} + \eta_a \quad (67)$$

and the reductive potential to apply to the system reads:

$$E = E_{i=0} - \eta_c \quad (68)$$

In these two equations,  $\eta_a$  is relative to the overpotential in the anodic region (oxidation) and  $\eta_c$  is relative to the overpotential in the cathodic region (reduction). These overpotential  $\eta_a$  and  $\eta_c$  could be measured by an electrochemical method. If  $\eta$  is small the system could be described as a fast electrochemical system whereas if  $\eta$  is big the electrochemical system is described as a slow system. Indeed a electrochemical system with a big overpotential is related to a slow electron transfer kinetic whereas a electrochemical system with a low overpotential is related to a fast electron transfer kinetics.

On a typical polarisation curve, two distinct regions can be observed. A first region where an increase of the applied potential leads to a stable current and a second region where an increase of the applied potential results in an exponential increase of the current. This first region is called the capacitive region, region in which no electrochemical reaction takes place. The second region is called the faradic region and relates to the occurrence of an electrochemical reaction.

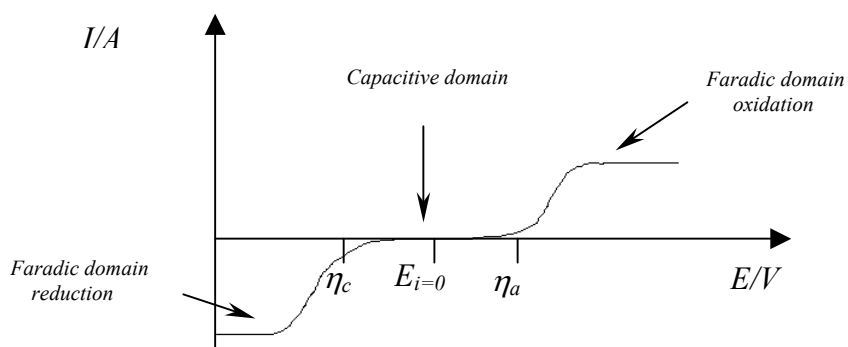


Figure 2: Polarisation curve of an organic specie

## IV.2. Fast and slow systems

As mentioned above, the over potential  $\eta$  is accessible by way of an electrochemical analysis. The two following polarisation curves show the difference between a slow and a fast electron transfer reaction:

Slow systems with big  $\eta$ :

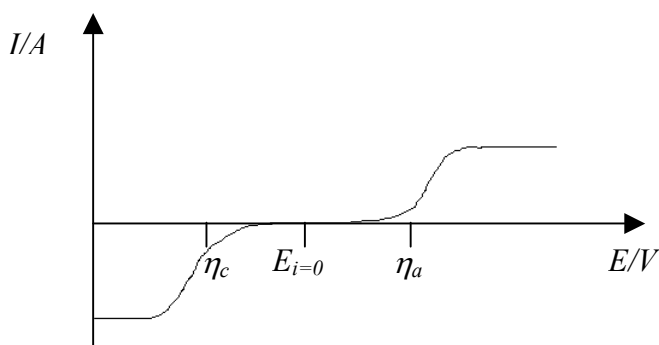


Figure 3: Polarisation curve of a slow electron transfer reaction

Fast systems with low  $\eta$ :

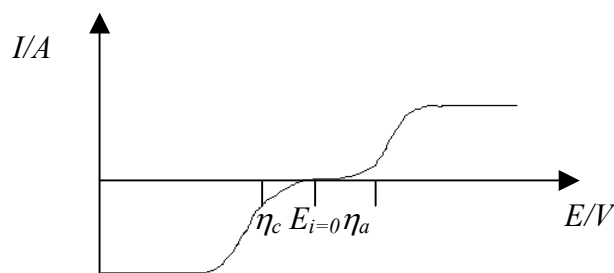


Figure 4: Polarisation curve of a fast electron transfer reaction

## V. Electroactive domains<sup>2</sup>

The electroactive domain of an organic species depends on the nature of the solvent in which the electrochemical reaction takes places, on the pH and composition of the solution and on the nature of the substituents born by the organic molecule.

### V.1. Electroactive domain for oxidable and reducible functions

By tacking in account all these parameters, a window of electroactivity can be determined for each class of organic molecules and we provide here and after an example found in the literature<sup>2</sup> for the main classes of molecules.

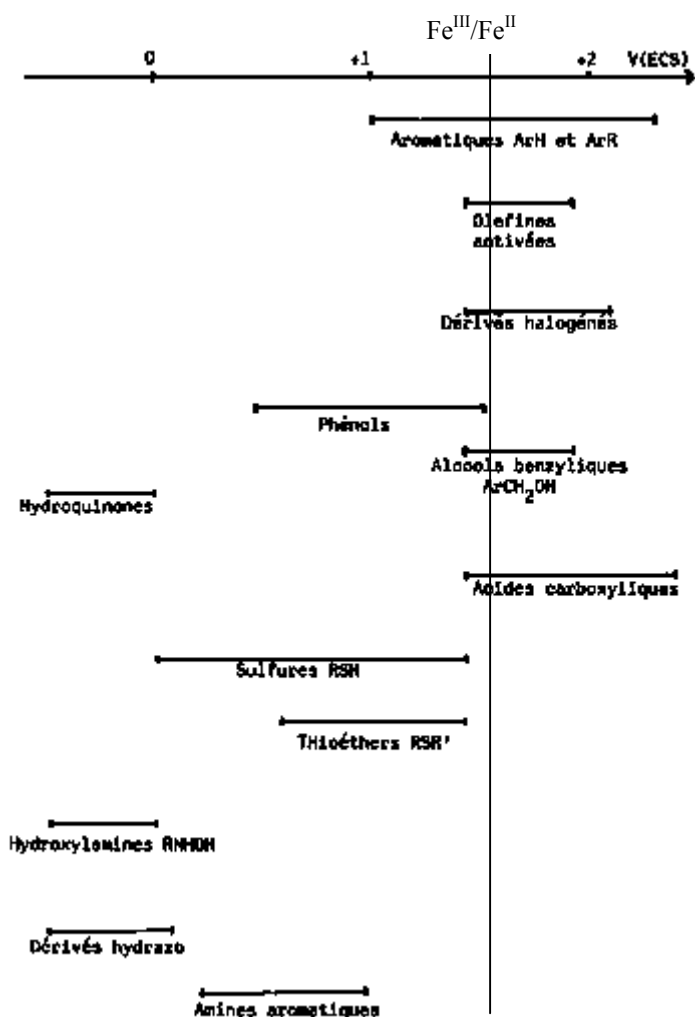


Figure 5: Electroactive domains in oxidation for the main classes of organic functions  
The vertical line represents the standard redox potential of ferri/ferrocyanide used as electrochemical probe

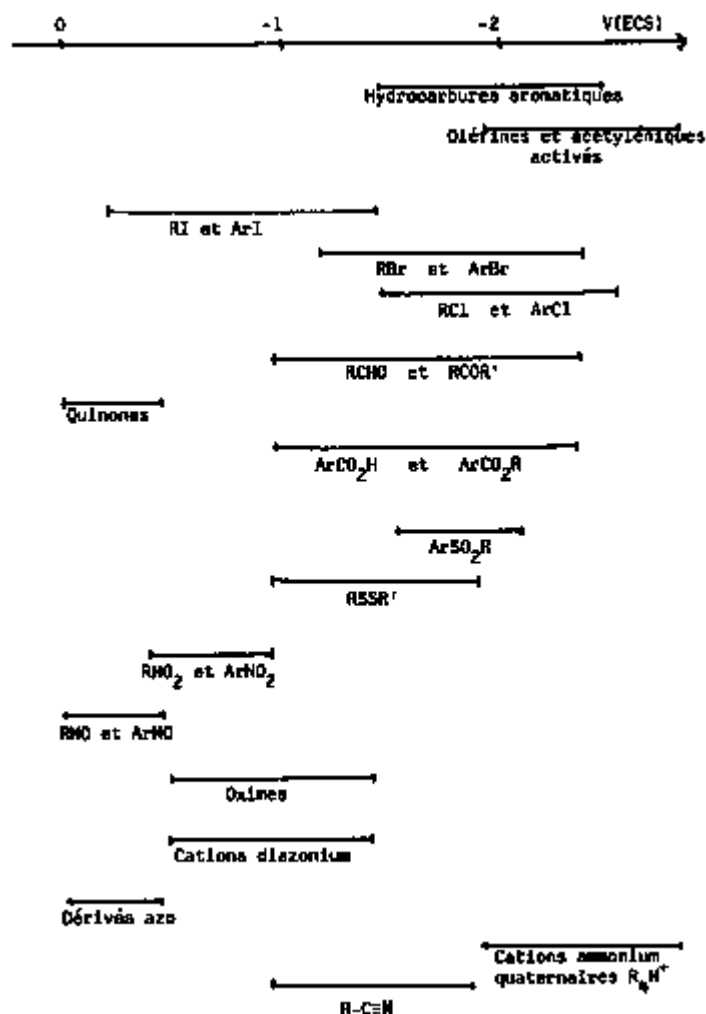


Figure 6: Electroactive domains in reduction for the main classes of organic functions

## V.2. The electroactive domain is related to the nature of the used solvent.

### V.2.1. Aqueous solvents

The electroactive domain of a specific compound is related to the solvent in which the electroactive molecule is dissolved. For example, if the standard redox potential of the studied molecule is found (in the practical textbooks) to be 1.8 V/NHE and if the electrochemical reaction is studied in water for which the standard potential for the oxidation into  $O_2$ ,  $E_{O_2/H_2O}^0$  is 1.23 V/NHE, this means that before showing the oxidation of the target molecule, the electrochemical experiments will show the oxidation of water. For organic redox couples having a standard redox potential above the one of water, the organic redox couple could not be studied in water.

The same constataction could be also addressed in reduction. If the studied redox couple possesses a standard redox potential below the one of water for which  $E_{H^+/H_2}^0$  is 0 V/NHE, it is not possible to reduce these organic species in water.

The possible accessible potential window in water is thus given by:

in oxidation

$$\text{H}_2\text{O}/\text{O}_2 \rightarrow E_{\text{O}_2/\text{H}_2\text{O}}^0 \text{ is } 1.23 \text{ V/NHE} \quad (69)$$

in reduction

$$\text{H}^+/\text{H}_2 \rightarrow E_{\text{H}^+/\text{H}_2}^0 \text{ is } 0 \text{ V/NHE} \quad (70)$$

These two standard potentials are taken at pH=0 and their values can vary a little bit depending on the nature of the used electrodes for the electrochemical study (see the following parts). The nature of the electrodes play a role on the value of the required over potential to oxidise or reduce the water.

In many cases, it is suitable to study the potential window of the solvent in which one wants to study the electrochemical activity of an organic species.

## V.2.2. Non aqueous solvents

Using organic solvent or a mixture of organic solvents, the accessible potential window could be greater or smaller than the one obtained in an aqueous solvent. The following table gives the accessible potential windows depending on the used solvent and the electrodes natures. In every cases, the adding salt, called the supporting electrolyte is used to increase the conductivity of the non aqueous solvent but plays no role on the electrochemical behaviour of the analysed specie.

|                                                  | Dielectric constant | Working electrode | Reference electrode | Supporting electrolyte | Anodic limit (V) | Working electrode | Reference electrode | Supporting electrolyte | Cathodic limit (V)      |
|--------------------------------------------------|---------------------|-------------------|---------------------|------------------------|------------------|-------------------|---------------------|------------------------|-------------------------|
| Water                                            | 80                  | Pt                | SCE                 | HClO <sub>4</sub>      | 1.5              | Hg                | SCE                 | TBAP                   | -2.7                    |
| Methanol                                         | 33                  |                   |                     |                        |                  | Hg                | Hg pool             | TEAB                   | -2.2 [423] <sup>c</sup> |
| H <sub>2</sub> SO <sub>4</sub> (96-99%)          | >84                 |                   |                     |                        |                  | Hg                | Hg pool             | None                   | -0.7 [216]              |
| CH <sub>3</sub> COOH                             | 6.2                 | Pt                | SCE                 | NaOAc                  | 2.0 [291]        | Hg                | SCE                 | TEAP                   | -1.7 [424]              |
| CH <sub>3</sub> CN                               | 37.5                | Pt                | Ag/Ag <sup>+</sup>  | LiClO <sub>4</sub>     | 2.4 [327]        | Pt                | Ag/Ag <sup>+</sup>  | LiClO <sub>4</sub>     | -3.5 [327]              |
| DMF                                              | 36.7                | Pt                | Hg pool             | LiClO <sub>4</sub>     | 1.5 [336]        | Hg                | Hg pool             | TEAP                   | -3.5 [336]              |
| NMP                                              | 32                  | Pt                | Hg pool             | LiClO <sub>4</sub>     | 1.4 [336]        | Hg                | Hg pool             | TEAP                   | -3.3 [336]              |
| HMPA                                             | 30                  | Pt                | Ag/Ag <sup>+</sup>  | LiClO <sub>4</sub>     | 0.8 [327]        | Hg                | Ag/Ag <sup>+</sup>  | LiClO <sub>4</sub>     | -3.6 [343]              |
| NH <sub>3</sub>                                  | 23                  |                   |                     |                        |                  | Hg, Pt            | Hg pool             | TBAI                   | -2.3 [205]              |
| (H <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>  | 12.5                | C                 | SCE                 | TEAP                   | 0.1 [292]        | Hg                | SCE                 | TEAP                   | -2.65 [292]             |
| Pyridine                                         | 13                  | Graphite          | Ag/Ag <sup>+</sup>  | LiClO <sub>4</sub>     | 1.4 [349]        | Hg                | Hg pool             | LiClO <sub>4</sub>     | -1.7 [349]              |
| DMSO                                             | 46.7                | Pt                | SCE                 | NaClO <sub>4</sub>     | 0.7 [347]        | Hg                | SCE                 | TEAP                   | -2.8 [347]              |
| Sulfolane                                        | 44                  | Pt                | SCE                 | NaClO <sub>4</sub>     | 2.3 [357]        | Pt                | SCE                 | NaClO <sub>4</sub>     | -4 [357]                |
| PC                                               | 69                  | Pt                | SCE                 | TEAP                   | 1.7 [370]        | Hg                | SCE                 | TEAP                   | -2.5 [370]              |
| CH <sub>3</sub> NO <sub>2</sub>                  | 36.7                | Pt                | SCE                 | LiClO <sub>4</sub>     | 2.7 [184]        | Hg                | SCE                 | LiClO <sub>4</sub>     | -1.2 [184]              |
| THF                                              | 7.4                 | Pt                | Ag/Ag <sup>+</sup>  | LiClO <sub>4</sub>     | 1.8 [223]        | Pt                | Ag/Ag <sup>+</sup>  | LiClO <sub>4</sub>     | -3.6 [223]              |
| (CH <sub>3</sub> OCH <sub>2</sub> ) <sub>2</sub> |                     | Hg                | SCE                 | TBAP                   | 0.65 [224]       | Hg                | SCE                 | TBAP                   | -2.95 [224]             |
| CH <sub>2</sub> Cl <sub>2</sub>                  | 8.9                 | Pt                | SCE                 | TBAP                   | 1.8 [262]        | Pt                | SCE                 | TBAP                   | -1.7 [262]              |

<sup>a</sup>The limit for the accessible potential for a solvent depends on many factors, such as supporting electrolyte, electrode material, and magnitude of permissible current density, and the numbers given are cited as illustrative values only.

<sup>b</sup>DMF = dimethylformamide; NMP = N-methylpyrrolidone; HMPA = hexamethylphosphotriamide; DMSO = dimethyl sulfoxide; sulfolane = tetramethylene sulfone; PC = propylene carbonate; THF = tetrahydrofuran; TBAP, TBAI = tetrabutylammonium perchlorate or iodide, respectively; TEAP, TEAB = tetraethylammonium perchlorate or bromide, respectively.

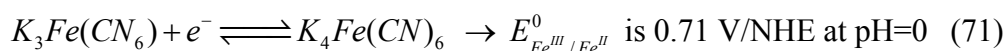
<sup>c</sup>Reference numbers.

Table 1: Influence of the solvent nature on the accessible potential window in oxidation and reduction

### V.3. Factors influencing the electroactive domain of an organic specie.

#### **V.3.1 Presence of a electrochemical mediator**

In the present case, the use of a mediator could be a limited factor. For example if the concentration of the mediator i.e. a ferri/ferrocyanide compound is larger than the concentration of the analyte (by a factor of 100), the potential window will be limited by the oxidation of  $Fe^{II}$  to  $Fe^{III}$  in the anodic region and by the reduction of  $Fe^{III}$  to  $Fe^{II}$  in the cathodic region. Considering now the standard redox potential of the two species in HCl 1M it comes:



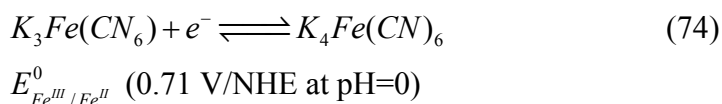
In such case the accessible potential window is different from the accessible potential window in water an means that an organic molecule having a standard redox potential upon 0.71 V/NHE at pH=0 can not be oxidised in presence of a high concentration of mediator. The same constatation could easily done in reduction. Due to the fast character of the electronic transfer of this redox couple, the potential window will be limited around 0.71 V/NHE.

#### **V.3.2. Reactions occurring between an organic specie and an electrochemical mediator.**

Another problem could arise when one use a redox mediator. It may occur that an organic redox couple could act as an oxidant or a reductant onto the redox couple chosen as mediator. Considering a redox couple used to monitor the current such as ferri/ferrocyanide:



When the studied organic compound is under an oxidise state, like a carboxylic acid for example, the organic compound can be reduced into an aldehyde by the mediator. This kind of reaction (oxido reduction) can only occurs if the standard redox potential of the organic compound (carboxylic acid/aldehyde)  $E_{Ox_1/Red_1}^0$  is grater than the standard redox potential of the mediator. In that case the two half electrochemical reactions can be written:



In that precise case, a reaction between  $Ox_1$  (i.e. carboxylic acid) and  $K_4Fe(CN)_6$  occurs producing  $Red_1$  (i.e. aldehyde) and increasing the concentration of  $K_3Fe(CN)_6$ . This reaction leads to the reduction of the organic compound.

To suppress this side reaction, it may be possible to use as electrochemical mediator only  $K_3Fe(CN)_6$  instead of the mixture of  $K_3Fe(CN)_6 / K_4Fe(CN)_6$ .

When the studied organic compound is under an reduce state, like an aldehyde for example, the organic compound can be oxidised into an carboxylic acid by the mediator. This kind of reaction (oxido reduction) can only occurs if the standard redox potential of the organic compound (carboxylic acid/aldehyde)  $E_{Ox_1/Red_1}^0$  is lower than the standard redox potential of the mediator. In that case the two half electrochemical reactions can be written:



$$E_{Fe^{III}/Fe^{II}}^0 \text{ (0.71 V/NHE at pH=0)}$$



In that precise case, a reaction between  $K_3Fe(CN)_6$  and  $Red_1$  (i.e. aldehyde) occurs producing  $Ox_1$  (i.e. carboxylic acid) and increasing the concentration of  $K_4Fe(CN)_6$ . This reaction leads to the oxidation of the organic compound.

To suppress this side reaction, it may be possible to use as electrochemical mediator only  $K_4Fe(CN)_6$  instead of the mixture of  $K_3Fe(CN)_6$  /  $K_4Fe(CN)_6$ .

In every cases, the oxido-reduction reaction is not only governed by the thermodynamics like mentioned above. Sometimes due to some kinetics aspects, such reaction which are favoured by the thermodynamics are not kinetically favoured and the reaction not occur. Only an experiment can give an answer.

## VI. Determination and variations of the standard redox potentials<sup>4,5,6</sup>

There is many possibilities to access the standard redox potential  $E_{Ox/Red}^0$  of an electroactive species even by using suitable textbooks or by performing an electrochemical measurement.

### VI.1. Determination of the standard redox potential using textbooks<sup>4,5,6</sup>

In many electrochemical text books, the values of the different standard potentials are given for many compounds. These  $E_{Ox/Red}^0$  are given for a certain pH, more often at pH= 0, for a certain temperature and versus the normal hydrogen electrode taking as a reference electrode. We will see in the next section that it is possible to correct the values of the standard redox potential with the pH of the solution as well as with another reference electrode.

### VI.2. Determination of the $E^0$ using electrochemical methods<sup>4,5</sup>

The  $E_{Ox/Red}^0$  of a redox couple can be also accessed by electrochemical methods such as cyclic voltammetry. In this case the voltamperogramme exhibits two waves corresponding to the oxidation and the reduction of the species. The two peaks for a reversible redox couple are separated by  $\Delta E_p = 59mV / n$  at  $25^\circ C$  in which  $n$  represents the number of electrons that the redox couple exchange. From a practical point of view, the  $E_{Ox/Red}^0$  is then given by:

$$E_{Ox/Red}^0 = \frac{1}{2}(E_{pa} + E_{pc}) \quad (77)$$

In the case of  $\Delta E_p$  greater than  $59mV / n$ , the electrochemical mechanism is considered as irreversible and we cannot access to the standard potential of the redox couple. The following cyclic voltammetry curves represent the oxidation and the reduction of a species:

In the case of a fast electron transfer, it is possible to access to the  $E_{Ox/Red}^0$  :

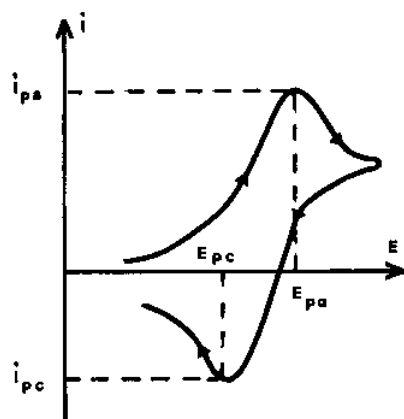


Figure 7: Cyclic Voltammogram of a reversible redox couple<sup>2</sup>

In the case of a slow electron transfer it is not possible to access to the  $E_{Ox/Red}^0$  :

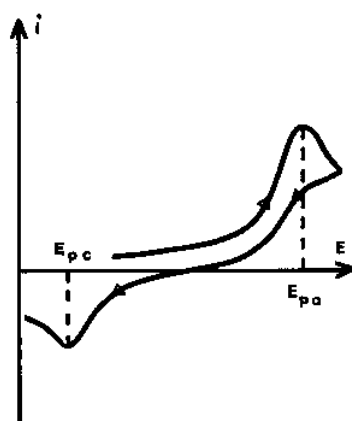


Figure 8 : Cyclic Voltammogram of a non-reversible redox couple<sup>2</sup>

## VI.3. Variation of standard redox potential of an organic specie

### VI.3.1. Influence of the nature of the reference electrode.

The value of the redox potentials found in the practical textbooks are often expressed versus the Normal Hydrogen Electrode NHE. When the determination of the redox standard potential is done by an electrochemical method, the most commonly used reference electrode is the Saturated Calomel Electrode SCE. The following table gives the correlation between the NHE and the SCE:

| T (°C)     | 0     | 10    | 20    | 25    | 30    | 40    | 50    |
|------------|-------|-------|-------|-------|-------|-------|-------|
| E (mV)/NHE | 259.2 | 253.9 | 247.7 | 244.5 | 241.2 | 234.5 | 227.4 |

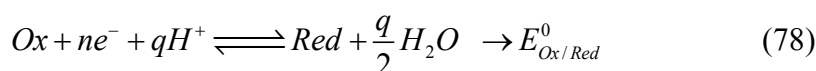
Table 2: Potentials of an SCE reference electrode versus the NHE reference electrode, Radiometer S.A. Copenhagen

For example, if a redox couple exhibits a standard redox potential of  $E_{Ox/Red}^0 = 1V$  vs NHE, this standard redox potential could be calculated using a saturated calomel electrode SCE as reference electrode. Using table 2, it comes  $E_{Ox/Red}^0 = 0.75 V/SCE$  at 25°C.

### VI.3.2. Influence of the pH of the solution<sup>7</sup>

When an electrochemical reaction involving a redox couple takes place by exchanging protons or hydroxyls, the value of the standard redox potential  $E_{Ox/Red}^0$  of the considered redox couple is affected by the presence of the protons or by the hydroxyls.

For example considering the following half electrochemical equation for a redox couple consuming protons, defined by  $E_{Ox/Red}^0$ :



Taking into account that the activity of water  $a(H_2O)$  is 1, the Nernst equation resulting from this half electrochemical equation is:

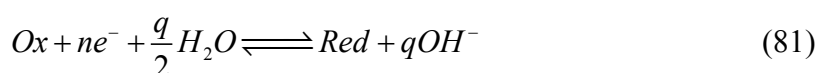
$$E_{i=0} = E_{Ox/Red, pH=0}^0 - \frac{2.3RT}{F} \left(\frac{q}{n}\right) pH + \frac{RT}{nF} \ln \frac{a(Ox)}{a(Red)} \quad (79)$$

The factor 2.3 comes from the transformation of Ln into Log.

The normal potential at a given pH for which  $a(Ox)=a(Red)=1$  by:

$$E_{Ox/Red, pH}^0 = E_{Ox/Red, pH=0}^0 - \frac{2.3RT}{F} \left(\frac{q}{n}\right) pH \quad (80)$$

For example considering the following half electrochemical equation for a redox couple leading to some hydroxyls:



The Nernst equation gives:

$$E_{i=0} = E_{Ox/Red, pH=0}^0 + \frac{2.3RT}{F} \left(\frac{q}{n}\right) pOH + \frac{RT}{nF} \ln \frac{a(Ox)}{a(Red)} \quad (82)$$

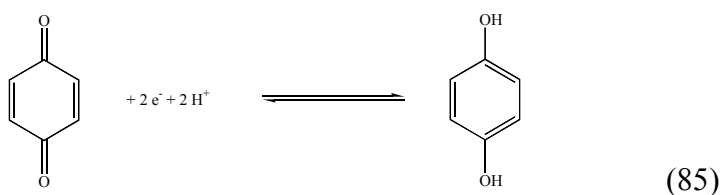
Taking in account that  $pOH + pH = 14$ , thus  $pOH = 14 - pH$ , it comes:

$$E_{i=0} = E_{Ox/Red, pH=0}^0 + \frac{2.3RT}{F} \left(\frac{q}{n}\right) (14 - pH) + \frac{RT}{nF} \ln \frac{a(Ox)}{a(Red)} \quad (83)$$

We could define a Normal potential at a given pH for which  $a(Ox) = a(Red) = 1$  by:

$$E_{Ox/Red, pH}^0 = E_{Ox/Red, pH=0}^0 - \frac{2.3RT}{F} \left(\frac{q}{n}\right) (14 - pH) \quad (84)$$

As an example, we can apply this equation to the electrochemical oxidation of hydroquinone into benzoquinone which is a proton consuming reaction. The redox couple Benzoquinone/Hydroquinone possesses a standard redox potential of 0.699 V/NHE at  $pH=0$ . The half electrochemical equation could be written as:



Applying the previously described relation, it comes:

$$E_{BQ/HQ, pH}^0 = E_{BQ/HQ, pH=0}^0 - \frac{2.3RT}{F} \left(\frac{2}{2}\right) pH \quad (86)$$

Replacing in this equation the value of each terms, it gives at 25°C:

$$E_{BQ/HQ, pH}^0 = 0.699 - 0.059 pH \quad (87)$$

As another example, we can give the different standard redox potentials of the couple  $K_3Fe(CN)_6 / K_4Fe(CN)_6$  at different pH in aqueous solution:

| Medium                                 | HCl 0.1M | HCl 1M | HClO <sub>4</sub> 1M |
|----------------------------------------|----------|--------|----------------------|
| $E_{Fe^{III}/Fe^{II}}^0$ V/NHE at 25°C | 0.56     | 0.71   | 0.72                 |

Table 3: Dependence of the standard redox potential of ferri/ferrocyanide with the pH

Sometimes it can be noted that the standard redox potential varies with the nature and the concentration of the supporting electrolyte used for the electrochemical measurements.

### VI.3.3. Influence of the nature of the substituents bearing by the organic specie<sup>8,9,10</sup>

The substituents present on an organic molecule can change the redox properties of the organic compound by an electronic effect. The substituent that influences the redox properties have to be conjugated to the redox site (mesomeric effect) or very close to the redox site (inductive effect). In general, an inductive effect is related to the motion of the  $\sigma$  electrons (atoms involved in a single bond) and vanishes after few bonds. The mesomeric effect concern the motion of the  $\pi$  electrons (atoms involved in a double or more bond) and the influence of this effect is more intense than the inductive effect. The substituents could be divided into two groups. Electrodonating and electroattracting groups.

The effect of these groups was well explored by Hammett which gave a constant in which the sign highlights the electrodonating or attracting effect of the substituent. A positive Hammett constant relates to an attractive effect and the value of this constant relates to the nature of this effect. Thus, a small value relates to an inductive effect whereas a big value is related to a mesomeric effect. In contrast, a negative Hammett constant is relates to a donating effect and the value as it was previously mentioned relates to the nature of this effect.

An electrodonating group tends to decrease the electronic density on the redox site. That means that this redox site is more difficult to oxidise but easier to reduce.

An electroattractive group tends to increase the electronic density on the redox site and this site is easier to oxidise and more difficult to reduce.

In general, we can give a summary of the principal group bearing such effect, In this summary I is refers to an inductive effect (donor +I, attractor -I) and M is refers to a mesomeric effect (donor +M, attractor -M)

#### Donnors groups:

CH<sub>3</sub> (+I), CH<sub>3</sub>O- (+M, -I), OH, OR (+M, -I), NH<sub>2</sub>, NHR, NR<sub>2</sub> (+M)

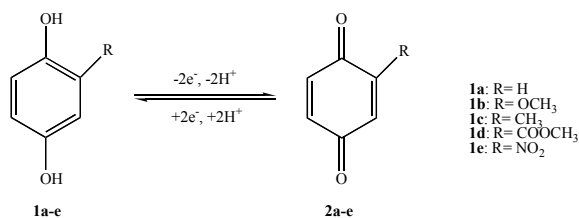
#### Neutral groups:

H, Cl (+M, -I), Br (+M, -I), I (+M, -I), Phenyl, SH, SR

#### Attractor groups

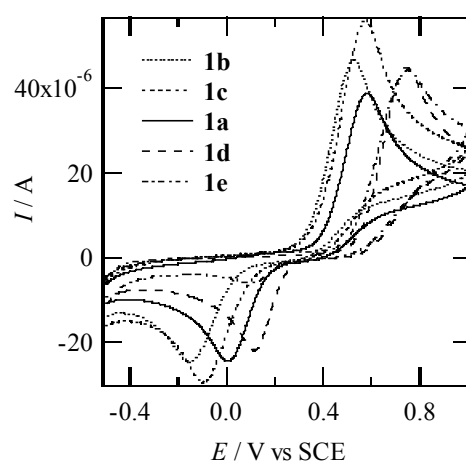
C=O (-M, -I), CH=O, (-M, -I), COOH (-M, -I), COR (-M, -I), COCl (-M, -I), O=C-O-O-R (-M, -I), O=C-O-O-C=O (-M, -I), CN (-M), NO<sub>2</sub> (-M)

As an example we can compare the oxidation of different hydroquinones bearing some electrodonating groups (CH<sub>3</sub>, CH<sub>3</sub>O) neutral group (H) and electroattractive groups (COOR, NO<sub>2</sub>). In theory, a donating group should decrease the oxidative potential of the benzoquinone ring whereas a electroattractive group should increase the oxidative potential of the hydroquinone ring. The oxidation of the hydrquinone can be described by the following electrochemical reaction:



(88)

This tendency is illustrated by the following electrochemical analyses realised by Cyclic voltammetry. The oxidation of the hydroquinones **1a-e** could be monitored by the position of the peak potential in the oxidative potential region (i.e  $E/V$  vs SCE > 0) and shows that the presence of a donor group (**1b** and **1c**) decreases the oxidative peak potential whereas the peak potential increases in presence of an attractor group (**1d** and **1e**). This voltamperometric method shows also that the mesomeric effect for **1b** is greater than the inductive effect of **1c** due to the fact that the oxidative potential of **1c** is more negative than the oxidative potential of **1b**.



Cyclic voltamperometric curves for hydroquinones **1a-e** recorder @ 75 mVs<sup>-1</sup> versus SCE (reference electrode)

## VII. Conclusion

This report gives a short overview of the different electroactive organic compounds and describes few items related to the thermodynamics and to the kinetics of the electron transfers occurring onto organic species. It was described also the different domains of electroactivity of each class of organic compounds. This report is not exhaustive and for more details, the references given in the bibliography part are good supports for electroorganic chemistry in general. We have focused on simple organic functions but complex structures like poly-functional molecules as well as heterocycles which constitute alone a very big and interesting part were not tackled.

## VIII. Bibliography

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