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TERMINOLOGY AND NOTATIONS FOR MULTISTEP ELECTROCHEMICAL REACTION MECHANISMS

(IUPAC Recommendations 1994)

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Terminology and notations for multistep electrochemical reaction mechanisms (IUPAC Recommendations 1994)

Abstract – Terminology and notations for a compact description of electrochemical reaction mechanism occurring at and near an electrode during the passage of current are given. These recommendations allow a detailed description of a sequence of chemical changes from a reactant to a particular product.

INTRODUCTION

In preceding reports of Commission I.3 (Electrochemistry) detailed definitions and recommendations for electrode reaction orders, transfer coefficients and rate constants were presented (ref. 1). These papers were focused on the kinetics of the process and did not give any recommendations for the description of either the mechanism of the electrochemical reaction, or the rate-determining step. These two last points must be accurately defined to give a complete description of the process and to properly design the experimental approach for elucidating the mechanism.

In the following paper, the recommended terminology and the use of symbols are given for a compact description of an electrochemical reaction mechanism, *i.e.* a theoretical sequence of chemical changes occurring at and near an electrode during the passage of current, from a reactant to a particular product. The electrochemical reaction mechanism must include at least one step in which charge is transferred from one phase to another (from the electrode to a species in solution or from the species to the electrode). This step is called the *charge transfer step*. It is accompanied by mass transport of the reactants and products to and from the electrode, and very often by chemical reactions, by other charge transfer steps at the electrode or in solution and by adsorption desorption reactions. The system for symbolic representation of reaction mechanisms (recommendation 1988) of the Commission on Physical Organic Chemistry (ref. 2) is used when it is not in opposition with some well established electrochemistry nomenclature.

A complete kinetic analysis of an electrochemical reaction would require determination of the complete mechanism and the rates of each of the corresponding steps. In the case of complicated processes this is very often not feasible but it is important to give the largest number of details. For example, what is the rate-determining step among the different steps under specified conditions (*i.e.* for well defined experimental conditions)? Such determinations are possible by the use of a variety of electrochemical techniques (refs. 3 and 4). Discussion of these methods is not the aim of this paper.

RECOMMENDED NOMENCLATURE FOR MULTISTEP ELECTROCHEMICAL REACTION MECHANISMS.

Since mass-transfer phenomena are involved in all electrochemical processes with the possible exception of purely interfacial reactions, mass-transfer steps are not specified in the compact notations for mechanisms. Successive events are indicated by the sign + and concerted ones without any separation.

Charge transfer at the electrode:

The symbol **E** represents a single one electron transfer. **E+E** corresponds to a transfer of two electrons to the same species without assuming simultaneous multiple electron transfer. Usually the fact that an oxidation or a reduction is involved, is not indicated, yet a process where two electron transfers occur in opposite directions (one reduction and one oxidation for example) is indicated as follows: $\mathbf{E}^{\rightarrow}$ for the first electron transfer and $\mathbf{E}^{\leftarrow}$ for the second one in the opposite direction.

Chemical reaction:

A chemical reaction occurring near or at the electrode is noted **C, C1** for first-order, **C1'** for pseudo first order-reaction (reaction $D + X \rightarrow F$ when X is in large excess as compared to D), **C2** for a second order reaction.

Special reactions are often specified by an abbreviation in parentheses
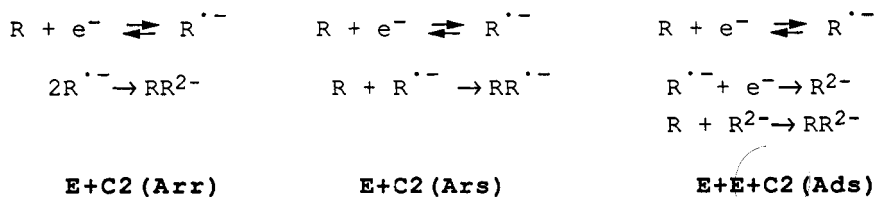
- a dissociation or bond-breaking is noted with **C1(D)** and an association or bond-forming with **C(A)**. A subscript is added, indicating a bond with a nucleophile (N), with an electrophile (E) or with a proton (H). Thus a protonation is noted **C(A$_H$)** (reaction $D + H^+ \rightarrow DH^+$ or reaction $D + SH \rightarrow DH^+ + S^-$) and a deprotonation **C(D$_H$)**.

- a dimerization process is often noted **DIM**. It is clearer to use:
 C2(Arr) if the dimerization occurs by coupling (association) of two species produced by the electron transfer (radicals (**r**) in the same oxidation state),
 **C2(Ars)** for a coupling between a reduced (or oxidized) radical species (**r**) and the substrate (**s**),
 C2(Ads) for a reaction between the substrate (**s**) and an intermediate obtained after a two-electron process, doubly reduced or oxidized (**d**).

$$R + e^- \rightleftharpoons R^{\bullet -} \qquad R + e^- \rightleftharpoons R^{\bullet -} \qquad R + e^- \rightleftharpoons R^{\bullet -}$$

$$2R^{\bullet -} \rightarrow RR^{2-} \qquad R + R^{\bullet -} \rightarrow RR^{\bullet -} \qquad R^{\bullet -} + e^- \rightarrow R^{2-}$$
$$R + R^{2-} \rightarrow RR^{2-}$$

E+C2(Arr) **E+C2(Ars)** **E+E+C2(Ads)**

- an electron transfer between two electrochemical couples in solution (solution electron transfer) is noted **T**
     Example: Redox catalysis of the reduction of A is named **E+T**:

$$R + e^- \rightleftharpoons R^{\bullet -}$$

$$R^{\bullet -} + A \rightleftharpoons R + A^{\bullet -}$$
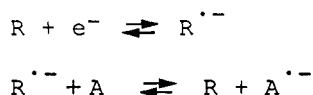
- a disproportionation (reaction of two identical species or two parent species in the same oxidation state to give one oxidized and one reduced product) is an important particular solution electon transfer noted **C2(T)**.

     Example: $\qquad R + e^- \rightleftharpoons R^{\bullet -}$

$$2R^{\bullet -} \rightarrow R + R^{2-}$$
$$\mathbf{E+C2(T)}$$
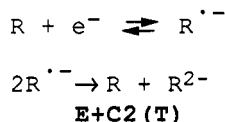
- For other complicated reactions, nomenclature described in ref. 2 can be used.

When it is possible to determine the reversibility or irreversibility of one or several chemical reactions, this fact is indicated as a subscript: **C$_{irr}$** or **C$_{rev}$**.

Adsorption-desorption reaction:

When chemical reactions occur in the adsorbed state, the same terminology is used with a subscript "ad"; for example **E+Cl$_{ad}$**. The adsorption-desorption step itself is not usually indicated; if it is a separated step, we suggest **Ad** for adsorption and **Ds** for desorption.

SOME COMMENTS ABOUT THE CHARGE-TRANSFER STEP AT THE ELECTRODE.

For a *simple charge transfer* i.e. for an elementary electron transfer without any other electrochemical or chemical step, the electrochemical process involves only mass transport phenomena coupled to the electron transfer. Yet, this elementary electron transfer must be defined by the nature of the reaction product. For example the product formed by a one electron reduction of a neutral molecule is not necessarily a radical anion with the same chemical formula, but it is possible that the electron uptake leads simultaneously to the cleavage of a chemical bond in the initial molecule. An electron transfer with simultaneous bond breaking and/or formation is called a *concerted transfer* and without any chemical bond formation or cleavage is called a *non-concerted transfer*. A *concerted electron transfer* must be very clearly differentiated from a process where the electron transfer is followed (or preceded) by a separate chemical reaction; in the case of a *concerted electron transfer*, the electron transfer and the bond cleavage (or formation) are simultaneous, without any formation of a transient intermediate. This terminology is introduced in preference to inner-sphere/outer-sphere transfer (refs. 5 and 6). The notation **E** is used for a non-concerted transfer, whereas **EA** and **ED** should be used for a concerted electron transfer and bond formation or bond cleavage respectively. It must be noted that the electrode itself can be considered as a non-concerted reagent when the electron is transferred without any particular interactions with the electrode (inert electrode) or as a concerted reagent when a chemical modification of electrode sites is involved in the process (frequently the case for a modified electrode).

In general the charge-transfer step for an electrochemical reaction is defined by its standard potential (E°) in the solution medium by comparison with an appropriate reference electrode in the same medium (refs. 7 and 8), and by its kinetic behaviour. Yet, even for a simple one electron charge transfer, the kinetic law cannot always be determined because, as indicated before, the electron transfer is accompanied by mass transfer. In a first approach, it is very useful to compare the kinetics of the overall process with the rate of mass transfer. In the case of *fast electron transfer*, the rate-limiting step should be mass transfer, thus making it impossible to estimate the electron transfer rate. A *slow electron transfer* corresponds to an experiment where, at least in a part of the experiment, the electron-transfer kinetics can be observed. It is necessary to emphasize that a conclusion of fast (or slow) electron transfer may well be a function of the experimental technique employed.

N.B. A fast electron transfer is often called "nernstian" due to the fact that equilibrium concentrations of two forms of the redox couple are essentially maintained at the electrode surface. This kind of behaviour is also often called an electrochemically reversible process and similarly a slow electron transfer is called an electrochemically irreversible or quasireversible process. The terms reversible and irreversible process, however, are not clearly defined and their meaning depends on the authors.
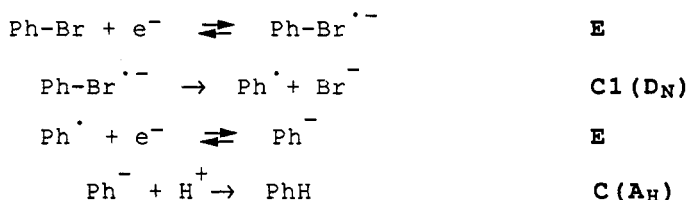
RATE-DETERMINING STEP:

Taking into account the experimental conditions it is possible to gain information on the rate-determining step. When it is useful to indicate this information and when it is clearly established, the rate-determining step is noted with a superscript double dagger. (Example **E+C$^{\neq}$**). It must be noted that this information corresponds to specified conditions and it will be necessary to use this notation only with a description of these conditions. Very often mixed kinetic control is obtained where two steps are involved in the rate of the overall process.

SOME EXAMPLES

The recommended nomenclature is shown by a few examples from the literature. The use of these examples does not mean that the proposed mechanisms are necessarily correct.
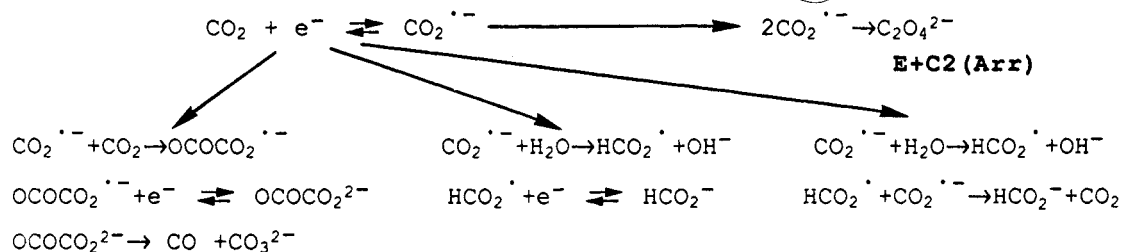
-Reduction mechanism of bromobenzene in dimethylformamide(ref. 9): **E+C+E** mechanism

$$Ph-Br + e^- \rightleftharpoons Ph-Br^{\bullet-} \qquad\qquad \textbf{E}$$

$$Ph-Br^{\bullet-} \rightarrow Ph^{\bullet} + Br^- \qquad\qquad \textbf{C1 (D}_\textbf{N}\textbf{)}$$

$$Ph^{\bullet} + e^- \rightleftharpoons Ph^- \qquad\qquad \textbf{E}$$

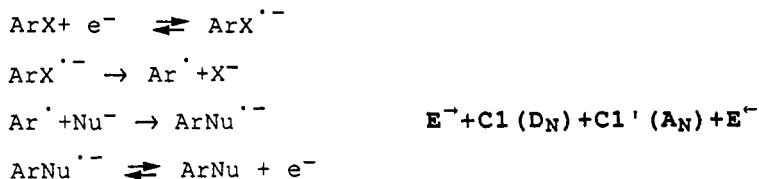$$Ph^- + H^+ \rightarrow PhH \qquad\qquad \textbf{C (A}_\textbf{H}\textbf{)}$$

The protonation is very often omitted because this step cannot be investigated in detail. It must be noticed that **E+C+E** is a very general notation for this kind of mechanism even with second-order chemical reactions.

When the above reaction is studied on a mercury electrode by linear sweep voltammetry in a sweep-rate range of 0.1-100 V/s at millimolar concentrations of substrate this mechanism is followed. Then the first electron transfer is the rate-determining step and this process can then be written:**E$^{\neq}$+C1$_\textbf{irr}$+E**.

- Some possible mechanisms for the reduction of carbon dioxide in aprotic medium (ref. 10):

$$CO_2 + e^- \rightleftharpoons CO_2^{\bullet-} \longrightarrow 2CO_2^{\bullet-} \rightarrow C_2O_4^{2-}$$

$$\textbf{E+C2 (Arr)}$$

$$CO_2^{\bullet-} + CO_2 \rightarrow OCOCO_2^{\bullet-} \qquad CO_2^{\bullet-} + H_2O \rightarrow HCO_2^{\bullet} + OH^- \qquad CO_2^{\bullet-} + H_2O \rightarrow HCO_2^{\bullet} + OH^-$$

$$OCOCO_2^{\bullet-} + e^- \rightleftharpoons OCOCO_2^{2-} \qquad HCO_2^{\bullet} + e^- \rightleftharpoons HCO_2^- \qquad HCO_2^{\bullet} + CO_2^{\bullet-} \rightarrow HCO_2^- + CO_2$$

$$OCOCO_2^{2-} \rightarrow CO + CO_3^{2-}$$

E+C2 (Ars) +E+C	**E+C1 (A$_\textbf{H}$) +E**	**E+C1 (A$_\textbf{H}$) +C2 (T)**

- Mechanism of first-order radical nucleophilic substitution (ref. 11): (Nu$^-$ is a nucleophile in high concentration):

$$ArX + e^- \rightleftharpoons ArX^{\bullet-}$$

$$ArX^{\bullet-} \rightarrow Ar^{\bullet} + X^-$$

$$Ar^{\bullet} + Nu^- \rightarrow ArNu^{\bullet-} \qquad\qquad \textbf{E}^-\textbf{+C1 (D}_\textbf{N}\textbf{) +C1' (A}_\textbf{N}\textbf{) +E}^-$$

$$ArNu^{\bullet-} \rightleftharpoons ArNu + e^-$$

-Reduction of carbonyl compound leading to pinacol in   protic medium (ref. 12):

$$RHC=O + H^+ \rightleftharpoons (RHC-OH)^+$$

$$(RHC-OH)^+ + e^- \rightleftharpoons (RHC-OH)^\cdot \qquad \textbf{C(A}_\textbf{H}\textbf{)+E+C2(Arr)}$$

$$2 (RHC-OH)^\cdot \rightarrow (RHCOH)_2$$
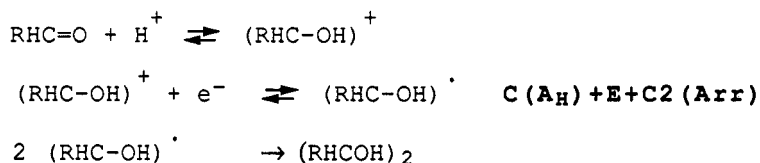
-Two possible mechanisms of reduction of protons at a platinum electrode (ref. 13):

$$H^+ + e^- \rightleftharpoons H_{ad}$$

$$2H_{ad} \rightarrow H_2 \qquad\qquad\qquad H_{ad} + H^+ \rightarrow H_2{}^+{}_{ad}$$

$$H_2{}^+{}_{ad} + e^- \rightleftharpoons H_2$$

$$\textbf{E+C2(Arr)}_\textbf{ad} \qquad\qquad \textbf{E+C2(Ars)}_\textbf{ad}\textbf{+E}$$
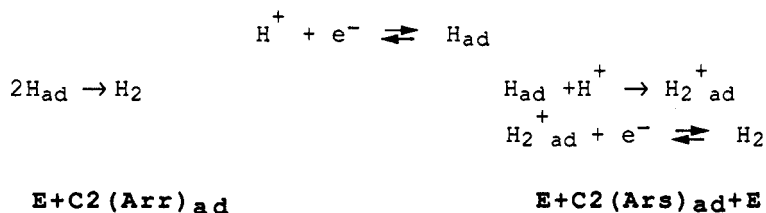
—   Direct and mediated reduction of some alkyl halides with a first concerted electron transfer (at the electrode or in solution)(ref. 14):

$$AX + e^- \rightleftharpoons A^\cdot + X^- \qquad\qquad R + e^- \rightleftharpoons R^{\cdot -}$$

$$A^\cdot + e^- \rightleftharpoons A^- \qquad\qquad R^{\cdot -} + AX \rightleftharpoons R + A^\cdot + X^-$$

$$A^- + H^+ \rightleftharpoons AH \qquad\qquad R^{\cdot -} + A^\cdot \rightleftharpoons R + A^-$$

$$A^- + H^+ \rightleftharpoons AH$$

$$\textbf{ED}_\textbf{N}\textbf{+E+C(A}_\textbf{H}\textbf{)} \qquad\qquad \textbf{E+TD}_\textbf{N}\textbf{+T+C(A}_\textbf{H}\textbf{)}$$
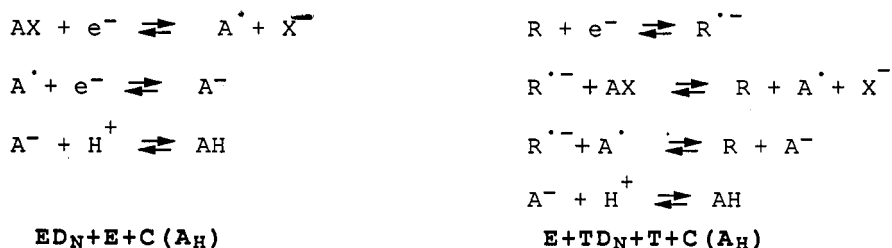
REFERENCES

1. R. Parsons, *Pure Appl. Chem.*, *37*, 503 (1974) and *52*, 233 (1980).
2. R. D. Guthrie, *Pure Appl. Chem.*, *61*, 23 (1989).
3. A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York (1980).
4. C. P. Andrieux and J-M. Savéant, *"Electrochemical Reactions" in Investigation of Rate and Mechanisms of Reactions, Techniques of Chemistry*, C. F. Bernasconi, Ed., Vol. VI, 4/E, Part 2. pp.350-390, Wiley, New York (1986).
5. R.A. Marcus,*J. Phys. Chem.*, *72*, 891 (1968).
6. J-M. Savéant., *"Single Electron Transfer and Nucleophilic Substitution" in Advances in Physical Organic Chemistry,* D. Bethell Ed., Vol 26, p. 1, Academic Press, London (1990).
7. A.J. Bard, R. Parsons and J. Jordan, *Standard Potentials in Aqueous Solution*, Dekker, New York (1985).
8. G. Gritzner and J. Kuta, *Pure Appl. Chem.*, *56*, 461 (1984).
9. C.P. Andrieux, C. Blocman, J-M. Dumas Bouchiat and J-M. Savéant, *J. Am. Chem. Soc.*, *101*, 3431 (1979).
10. C. Amatore and J-M. Savéant, *J. Am. Chem. Soc.*, *103*, 5021 (1981)
11. J-M. Savéant, *Acc. Chem. Res.*, *13* , 323 (1980).
12. M. M. Baizer and H. Lund, *Organic Electrochemistry,* Dekker, New York (1983).
13. R. R. Adzic, *"Electrocatalytic Properties of the Surfaces Modified by Foreign Metals" in Advances in Electrochemistry and Electrochemical Engineering*, H. Gerischer and C. W. Tobias Eds, Vol 13, p. 238, Wiley, New York (1984).
14. C.P. Andrieux, I. Gallardo, J-M. Savéant and K.B. Su, *J. Am. Chem. Soc.*, *108*, 638 (1986).