Electrochimica Acta 55 (2010) 8336–8340

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

The autoprotonation in reduction mechanism of pesticide ioxynil

Romana Sokolová[a,*,1], Magdaléna Hromadová[a,1], Jiří Ludvík[a,1], Lubomír Pospíšil[a,1], Stefania Giannarelli[b]

[a] J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague, Czech Republic
[b] Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56100 Pisa, Italy

ARTICLE INFO

Article history:
Received 23 November 2009
Received in revised form 21 January 2010
Accepted 22 January 2010
Available online 2 February 2010

Keywords:
Autoprotonation
Organic halides
Reduction
Pesticides
Polarography

ABSTRACT

The reduction mechanism of ioxynil (3,5-diiodo-4-hydroxy-benzonitrile) was studied in dimethylsulfoxide using the electrochemical methods (tast polarography, cyclic voltammetry and controlled potential electrolysis) combined with GC/MS identification of products. The reduction is accompanied by the cleavage of iodide yielding 3-iodo-4-hydroxybenzonitrile. Surprisingly, this process requires only one electron for the exhaustive electrolysis of the starting compound. We showed that the apparent one electron reduction observed in the aprotic solvent is due to the autoprotonation by another molecule of ioxynil. The overall one electron reduction (uptake of two electrons per two molecules of ioxynil) is changed in the presence of a strong proton donor to a two electron process per one molecule.

1. Introduction

Ioxynil (3,5-diiodo-4-hydroxy-benzonitrile) belongs to the group of benzonitrile herbicides, which inhibit the Photosystem II receptor site of green plants [1,2]. Only a few papers in the literature deal with the decomposition of these compounds. The reductive dehalogenation is an important pathway for the degradation of this pesticide by *Desulfitobacterium chlororespirans* [3]. The photohydrolysis of a carbon halogen bond leading to a monohalogenated dihydroxybenzonitrile was studied in the aqueous solution by Malouki et al. [4]. The electrochemical reduction of three 3,5-dihalogeno-4-hydroxy-benzonitrile compounds in dimethylsulfoxide was the subject of our previous report [5]. It was found that these compounds are reduced to an anion radical followed by the cleavage of the carbon–halogen bond. This interpretation was based on the electrochemical detection of halide anions formed in the process and by the detection of dehalogenated products by GC–MS method.

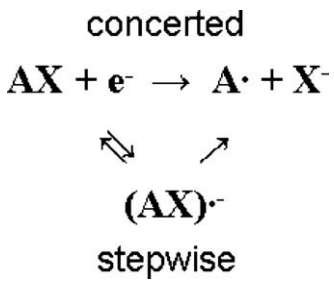
The reductive cleavage of a series of organic halogenides, including halogenoaromatics, benzyl halogenides and halogenoalkanes has been extensively studied in the literature [6–20]. It has been shown that the rate of cleavage of the halide ion from the anion radical decreases in the order I > Br > Cl > F. The process of dissociative electron transfer (DET) may occur in a concerted mechanism yielding directly an aryl radical or in a stepwise mechanism going through the formation of an anion radical as the intermediate (see Scheme 1) [13]. The overall reduction mechanism is influenced by the presence of a proton donor, the solvent and substituents on the aromatic ring.

The number of electrons consumed during the reductive cleavage of halide anions from halogenoaromatics reported in the literature is not consistent [21–28]. Jaworski et al. found the one electron concerted process for 1-chloro-10-methyltribenzotriquinacene in acetonitrile and DMF, whereas a two electron reduction involving DISP1 mechanism for the same compound in benzonitrile was observed [23].

Coupled chemical reactions often involve protonation steps. Protons are provided either by the added acids, by the solvent or even by the parent molecule. The latter process, called autoprotonation, was indeed found in the reduction of phthalimides [29] and hydroxyimines [30]. The overall stoichiometry of the reduction of hydroxyimines involved the exchange of two thirds of an electron per molecule. In this case the autoprotonation by the original reactant occurs twice. One proton exchange involves the "father–son" (starting molecule–anion radical) step and the second is the protonation of the resulting anion by the starting molecule. Another example of the autoprotonation mechanism comes from the substituted acetophenones, where arylanion formed in the ECE/DISP process reacts with starting molecule [31]. In the reduction mechanism of p-nitrobenzoic acid the self-protonation occurs not only in the "father–son" step, but also through the protonation of arylanion and other intermediates. The overall number of electrons involved in the first reduction is 0.8 [32]. The complicated reduc-

* Corresponding author.
E-mail address: sokolova@jh-inst.cas.cz (R. Sokolová).
[1] ISE member.

0013-4686/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2010.01.094



Scheme 1.

tion mechanism of halogenated pyrimidines in acetonitrile, which involves the regeneration of the original molecule in a disproportionation (DISP) process, was studied in the absence and presence of a proton donor. The authors found for 5-bromopyrimidine the change in the number of electrons from 1.12 to 2.0 [27].

The reduction of halogenated aromatics follows Scheme 1. Since this scheme yields both $A^{\bullet}$ and $AX^{\bullet-}$ species, two possible follow-up reaction pathways should be considered. Radical $A^{\bullet}$ can be directly reduced to A^- by the second electron

$$A^{\bullet} + e^- \rightleftarrows A^- \quad (1)$$

Alternatively, a disproportionation step can participate in the mechanism

$$A^{\bullet} + (AX)^{\bullet-} \rightarrow A^- + AX \quad (2)$$

Both reactions (1) and (2) finally yield the aryl anion A^-. The protonation of A^- leads to the final product

$$A^- + SH \rightarrow AH + S^- \quad (3)$$

The overall stoichiometry involves two electrons per molecule and the ratio between the starting compound and proton donor is 1:1

$$AX + 2e^- + SH \rightarrow AH + X^- + S^- \quad (4)$$

Such a reduction mechanism was found for halogenated acetophenones [31]. The protonation can proceed also by the hydrogen atom transfer (HAT) mechanism [12,17,28,29,33,34].

In this communication we report on the reduction of ioxynil in dimethylsulfoxide solvent in the absence and presence of added proton donor. We will demonstrate the presence of autoprotonation in the reduction of ioxynil and its role in the observation of an apparent one electron polarographic wave in our previous report [5].

2. Experimental

2.1. Reagents

Ioxynil (3,5-diiodo-4-hydroxybenzonitrile) was purchased as a pesticide reference material from Dr. Ehrenstorfer, GmbH (Augsburg, Germany). Tetrabutylammonium hexafluorophosphate (Sigma) was used as a supporting electrolyte and dried before use. Dimethylsulfoxide (DMSO, content of $H_2O < 0.005\%$, Aldrich) was used as received. All reagents and chemicals were used without any further purification.

2.2. Methods

Electrochemical measurements were done using an electrochemical system for cyclic voltammetry and tast polarography. It consisted of a fast rise-time potentiostat and a lock-in amplifier (Stanford Research, model SR830). The instruments were interfaced to a personal computer via an IEEE-interface card (AdvanTech, model PCL-848) and a data acquisition card (PCL-818) using 12-bit precision. A three-electrode electrochemical cell was used with an Ag|AgCl|1 M LiCl reference electrode (with potential 0.210 V vs. SHE) separated from the test solution by a salt bridge. The working electrode was a valve-operated static mercury electrode (SMDE2, Laboratorní Přístroje, Prague) with an area 1.13×10^{-2} cm^2 and mechanically controlled drop time 2 s. The auxiliary electrode was cylindrical platinum net. Oxygen was removed from the solution by passing a stream of argon.

The reduction products of ioxynil were obtained by exhaustive electrolysis of its 1.6×10^{-3} M solution in DMSO. The electrolysis on the mercury pool was performed at the potential of the limiting current of the first polarographic wave. A 6890 gas chromatograph (Agilent Technologies) equipped with a quadrupole mass spectrometric detector (at 150 °C), model 5973N (electron impact 70 eV, ion source 230 °C, interface temperature 280 °C), was used for GC/MS analysis of the reduction products. The amount of 2 μl of the electrolysed solution was injected into the GC/MS spectrometer. The supporting electrolyte did not interfere with the analysis. The chromatographic separation was performed on a 5% phenyl-95% methylpolysiloxane HP-5MS chemical-bonded fused silica capillary column (Hewlett-Packard) of 30 m length, 0.25 mm internal diameter, and 0.25 μm film thickness. Helium of 99.995% purity was used as a carrier gas. The initial temperature was 80 °C, then a temperature increase of 4 °C min^{-1} up to 290 °C was applied, followed by an isothermal period of 10 min. The injector (splitless mode) was kept at 250 °C.

3. Results and discussion

We reported previously the reduction products of three 3,5-dihalogeno-4-hydroxy-benzonitrile compounds [5]. The reduction behaviour is influenced by the nature of the halogen atom on the aromatic ring. The half-wave potentials of tast polarographic wave shift towards more negative values in the order I > Br > Cl. Surprisingly, the electric charge required for a complete electrolysis at the potential of the first reduction corresponds to the consumption of only one electron per molecule. It is probable that the controversy between the consumed charge and formed products originates from the participation of protonation reactions. For this reason we scrutinised the present system in the presence of various proton donors. The apparent one electron reduction process of ioxynil in aprotic media is changed in the presence of a strong proton donor. The potassium tetraoxalate was chosen as the best proton donor, because its first reduction wave occurs at −1.17 V, which does not interfere with the first reduction wave of ioxynil. Fig. 1 shows the tast polarogram of ioxynil in the presence of different concentrations of potassium tetraoxalate. The limiting current of polarographic wave increases with increasing concentration of the proton donor. The height of the reduction wave reaches the limiting value corresponding to two electrons at the ratio of ioxynil and tetraoxalate equal to 1:2 (Fig. 2A). This implies that in the presence of a sufficient proton donor concentration the mechanism involves the uptake of two electrons and two protons. The consumption of two electrons was confirmed by the controlled potential electrolysis. With the increasing concentration of tetraoxalate the half-wave potential (Fig. 2B) is shifted to more negative values. This indicates that the rate determining step of the whole process is an irreversible following chemical reaction involving the protonation step. When the concentration ratio of ioxynil to the potassium tetraoxalate reaches 1:2, the half-wave potential becomes independent of the tetraoxalate concentration and attains the limiting value $E_{1/2} = -0.923$ V. Thus the experimental observation indicates that the reduction has to involve two electrons and two protons.

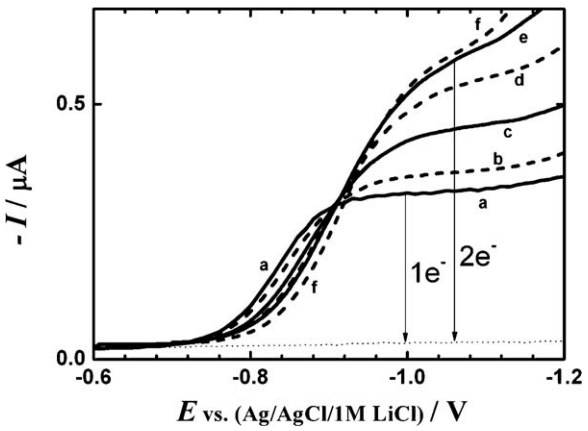


Fig. 1. Tast polarogram of 2.5×10^{-4} M ioxynil in 0.1 M $TBAPF_6$ and DMSO at different concentrations of potassium tetraoxalate: (a) 0, (b) 4.3×10^{-5} M, (c) 1.4×10^{-4} M, (d) 2.9×10^{-4} M, (e) 4.3×10^{-4} M and (f) 7.0×10^{-4} M. Drop time was 1.5 s. Dotted line represents the tast polarogram of the supporting electrolyte.

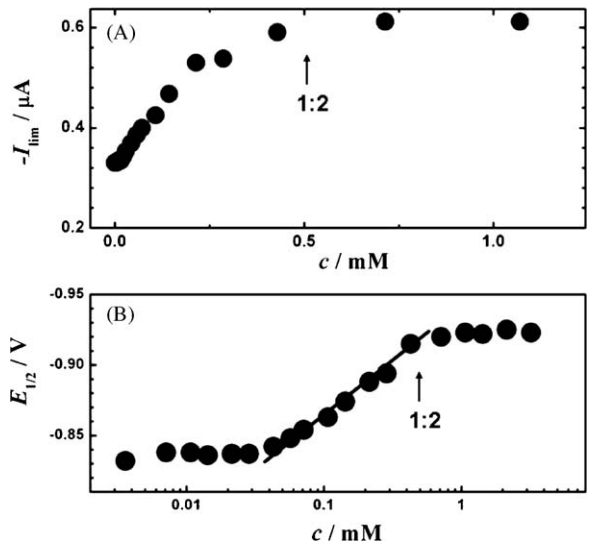


Fig. 2. The dependence of the limiting current (A) and the half-wave potential (B) of the polarographic curves of 2.5×10^{-4} M ioxynil in 0.1 M $TBAPF_6$ and DMSO on the concentration of potassium tetraoxalate.

Under the conditions when no proton donor is present in the solution we found that the reduction of ioxynil proceeds with the consumption of one electron per molecule, which was obtained by the exhaustive electrolysis at the potential of the first polarographic wave (see Fig. 3). It is likely that the hydroxyl group of the starting molecule provides the necessary proton for the reduction process. The height of the first reduction wave of ioxynil is linearly dependent on the concentration of the reactant. This excludes the participation of a bimolecular reaction of the 'father–son' type.

We suppose that the reduction process follows Scheme 2. The rate determining step is the cleavage of halogen anion (see Eq. (11)), which was identified as one of the reduction products [5]. The peak width of the first reduction wave measured by cyclic voltammetry $|E_p - E_{p/2}| = 72$ mV gives the value of transfer coefficient 0.66 (cal-

$$AX_2H + e^- \rightleftarrows (AX_2H)^{\cdot -} \quad (10)$$

$$(AX_2H)^{\cdot -} \rightarrow AXH^{\cdot} + X^- \quad (11)$$

$$AXH^{\cdot} + e^- \rightleftarrows AXH^- \quad (12)$$

$$AXH^- + AX_2H \rightarrow AXH_2 + AX_2^- \quad (13)$$

$$2\,AX_2H + 2e^- \rightarrow AXH_2 + AX_2^- + X^- \quad (14)$$

$$AXH^{\cdot} + AX_2H \rightleftarrows AXH_2 + AX_2^{\cdot} \quad (15)$$

$$AX_2^{\cdot} + e^- \rightleftarrows AX_2^- \quad (16a)$$

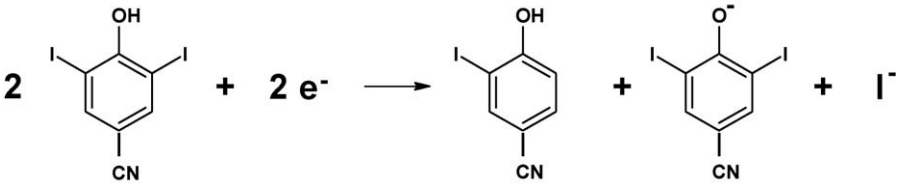
and/or

$$AX_2H + e^- \rightleftarrows (AX_2H)^{\cdot -} \quad (16b)$$

$$AX_2^{\cdot} + (AX_2H)^{\cdot -} \rightarrow AX_2^- + AX_2H$$

$$2\,AX_2H + 2e^- \rightarrow AXH_2 + AX_2^- + X^- \quad (17) \equiv (14)$$

Scheme 2.



Scheme 3.

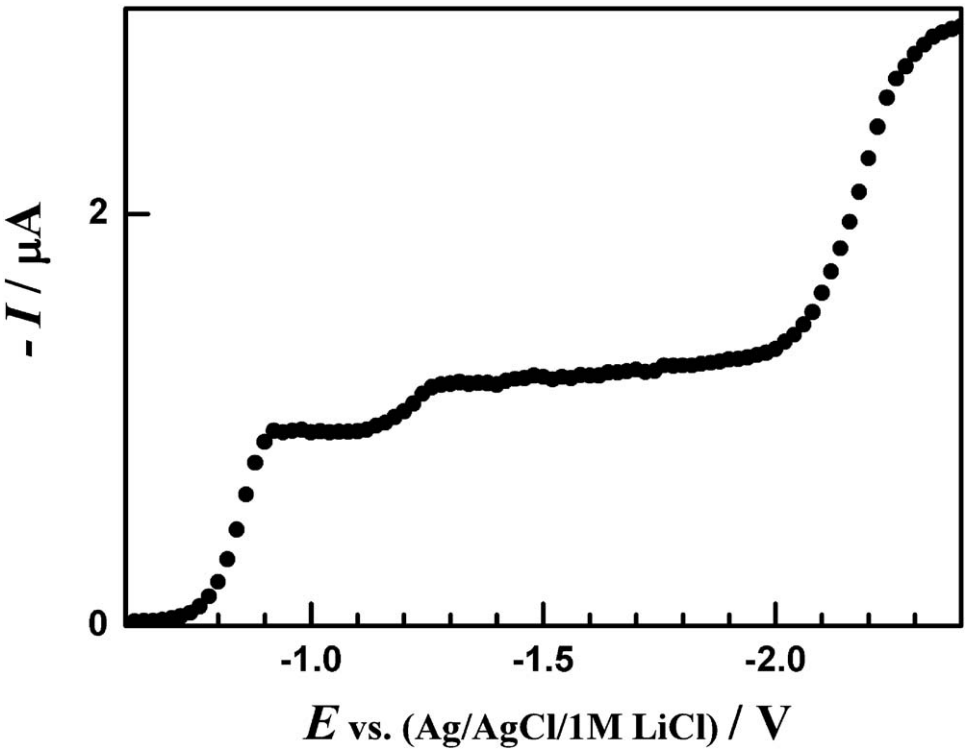


Fig. 3. Tast polarogram of 1.5×10^{-3} M ioxynil in 0.1 M $TBAPF_6$ and DMSO. Drop time was 1.5 s.

culated from the peak width: $|E_p - E_{p/2}| = 1.857\,RT/\alpha F$ [35]). On the voltammetric time scale the normalized current $I_p/v^{1/2}$ decreases with the increasing scan rate v (data not shown). The value of transfer coefficient α is higher than 0.5 indicating a stepwise cleavage mechanism with the kinetic control by a chemical reaction (see Scheme 1). Halogenated aromatic compounds are known to obey such a stepwise mechanism [13]. The aryl radical formed by the cleavage of halide anion undergoes immediately the second electron transfer in the overall ECE type reaction (Eq. (12)). The anion AXH^- is protonated by the starting molecule (Eq. (13)) and *the number of electrons is two per two molecules* of ioxynil (Eq. (14)). The hydrogen atom transfer (HAT) (Eqs. (15) and (16)) can compete with the second electron transfer followed by the protonation (Eqs. (12) and (13)) and this process has the same stoichiometry (Eq. (17)). It is not generally easy to distinguish between ECE and HAT type of mechanism. HAT is favored for lower rate of the halide ion cleavage [34]. The experimental findings of the consumption of two electrons per two molecules do not help us to distinguish between these two pathways. On the contrary to a simple father–son proton exchange, the mechanism in Scheme 2 indicates first the dehalogenation step and then the proton transfer from starting molecule of ioxynil (AX_2H) to a dehalogenated intermediate (AXH^-). The overall reduction mechanism indeed involves two molecules of ioxynil as is shown for ioxynil in Scheme 3. The reduction wave of dehalogenated product 3-iodo-4-hydroxybenzonitrile occurs at −1.22 V (see second reduction wave in tast polarogram in Fig. 3). The polarographic wave at −2.18 V belongs to the reduction of hydroxybenzonitrile part of ioxynil [5]. Since the rate of the formation of intermediates is so fast that we can see their reduction waves even on the time scale of tast polarography (see Fig. 3), the ECE mechanism followed by an autoprotonation step is the most probable reaction pathway.

The GC–MS analysis of the products after exhaustive electrolysis at potential $E = -1.0$ V also gives support to the autoprotonation mechanism. Two main products were detected: 3-iodo-4-hydroxybenzonitrile and 3,5-diiodo-4-butoxybenzonitrile. The formation of 3,5-diiodo-4-butoxybenzonitrile can be explained by the reaction of phenolate anion with butyl presented in the supporting electrolyte $TBAPF_6$. The presence of butylated ioxynil and dehalogenated product was found in the ratio roughly 1:1 (see Fig. 4). This fact undoubtedly confirms the donation of proton from the hydroxy group. The autoprotonation step in solution not containing other proton donors was further confirmed by the addition of KOH. The formation of phenolate from ioxynil in the presence of KOH is accompanied by the release of H_2O. It was necessary to trap water by the activated molecular sieve, which was added to the cell in order to drive the conversion of ioxynil to phenolate. Indeed the addition of KOH and molecular sieve leads to a decrease and finally a complete disappearance of the reduction wave of ioxynil. We can conclude that the hydroxy group of ioxynil is a sufficient supplier of protons for the reduction of half of the amount of ioxynil. This is another confirmation of the autoprotonation in

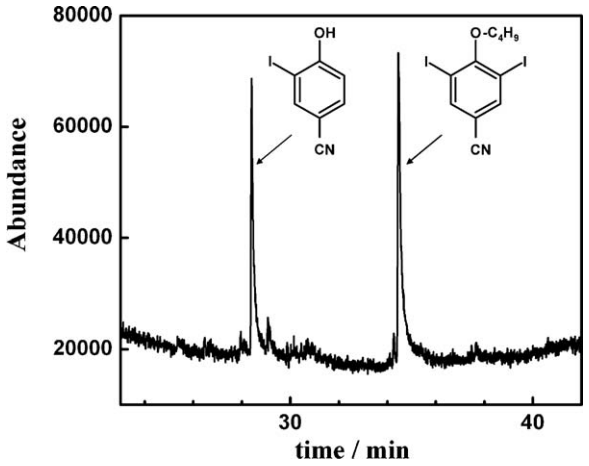


Fig. 4. Gas chromatogram of the solution of 3×10^{-3} M ioxynil in 0.1 M $TBAPF_6$ and DMSO after the exhaustive electrolysis at potential −1.0 V.

the overall reduction mechanism of ioxynil. The half of the ioxynil molecules provides the necessary protons for a two electron reduction of ioxynil as shown in Scheme 3. The two electron exhaustive electrolysis in the presence of tetraoxalate yields exclusively 3-iodo-4-hydroxybenzonitrile. No butylated ioxynil was found.

4. Conclusions

The redox activity of halogenated hydroxybenzonitrile compounds has been investigated in aprotic media. The polarographically and coulometrically observed one electron consumption per one molecule of ioxynil is explained by the autoprotonation step in its reduction mechanism. In effect, the process is a two electron reduction involving only one half of the starting material. If the source of the protons is other than the starting molecule, all ioxynil is being converted to the dehalogenated product. The controlled potential coulometry in the presence of the strong proton donor confirms that two electrons are involved in the reduction process.

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic (203/09/1607 and 203/08/1157) and Ministry of Education (LC510 and COST OC140).

References

[1] C.D.S. Tomlin, The Pesticide Manual, 12th ed., British Crop Protection Council, Farnham, UK, 2000, pp. 110–548.
[2] R. Sokolová, M. Hromadová, L. Pospíšil, in: M.P. Colombini, L. Tassi (Eds.), New Trends in Analytical, Environmental and Cultural Heritage Chemistry, Research Signpost, 2008, p. 43.
[3] A.M. Cupples, R.A. Sanford, G.K. Sims, Appl. Environ. Microbiol. 71 (2005) 3741.
[4] M.A. Malouki, A. Zertal, B. Lavédrine, T. Sehili, P. Boule, J. Photochem. Photobiol. A: Chem. 168 (2004) 15.
[5] R. Sokolová, M. Hromadová, J. Fiedler, L. Pospíšil, S. Giannarelli, M. Valášek, J. Electroanal. Chem. 622 (2008) 211.
[6] C.P. Andrieux, J.M. Savéant, K.B. Su, J. Phys. Chem. 90 (1986) 3815.
[7] G.V. Gavrilova, A.A. Moiseeva, E.K. Beloglazkina, A.A. Gavrilov, K.P. Butin, Russ. Chem. Bull. Int. Ed. 55 (2006) 1617.
[8] A.A. Isse, S. Gottardello, C. Durante, A. Gennaro, Phys. Chem. Chem. Phys. 10 (2008) 2409.
[9] J. Gassman, J. Voss, Z. Naturforsch. 63b (2008) 1291.
[10] J.W. Sease, F.G. Burton, S.L. Nickol, J. Am. Chem. Soc. 90 (1968) 2595.
[11] W.W. Hussey, A.J. Diefenderfer, J. Am. Chem. Soc. 89 (1967) 5359.
[12] J.M. Savéant, Bull. Soc. Chim. Fr. 2 (1988) 225.
[13] C.P. Andrieux, A. Le Gorande, J.M. Savéant, J. Electroanal. Chem. 371 (1994) 191.
[14] C.P. Andrieux, A. Le Gorande, J.M. Savéant, J. Am. Chem. Soc. 114 (1992) 6892.
[15] L. Eberson, Acta Chem. Scand. 53 (1999) 751.
[16] A. Muthukrishnan, M.V. Sangaranarayanan, J. Electrochem. Soc. 156 (2009) F23.
[17] M. Rejňák, J. Klíma, J. Svoboda, J. Ludvík, Collect. Czech. Chem. Commun. 69 (2004) 242.
[18] S. Antonello, F. Maran, J. Am. Chem. Soc. 120 (1998) 5713.
[19] A. Gennaro, A.A. Isse, C.L. Bianchi, P.R. Mussini, M. Rossi, Electrochem. Commun. 11 (2009) 1932.
[20] C. Costentin, M. Robert, J.-M. Savéant, Chem. Phys. 324 (2006) 40.
[21] M.A. Prasad, M.V. Sangaranarayanan, Chem. Phys. Lett. 414 (2005) 55.
[22] K.J. Houser, D.E. Bartak, M.D. Hawley, J. Am. Chem. Soc. 95 (1973) 6033.
[23] J.S. Jaworski, M. Cembor, B. Stępień, G. Häfelinger, Electrochim. Acta 51 (2006) 2322.
[24] J.S. Jaworski, M. Cembor, D. Kuck, Electrochim. Acta 52 (2007) 2196.
[25] D.G. Peters, in: H. Lund, O. Hammerich (Eds.), Halogenated Organic Compounds in Organic Electrochemistry, Marcel Dekker Inc., New York, 2001, p. 341.
[26] H. Jensen, K. Daasbjerg, Acta Chem. Scand. 52 (1998) 1151.
[27] C. Ji, D.G. Peters, E.R. Davidson, J. Electroanal. Chem. 500 (2001) 3.
[28] F. M'Halla, J. Pinson, J.-M. Savéant, J. Am. Chem. Soc. 102 (1980) 4120.
[29] C. Amatore, G. Capobianco, G. Farnia, G. Sandona, J.-M. Savéant, M.G. Severin, E. Vianello, J. Am. Chem. Soc. 107 (1985) 1815.
[30] A.A. Isse, A.M. Abdurahman, E. Vianello, J. Chem. Soc., Perkin Trans. 2 (1996) 597.
[31] C.P. Andrieux, J.M. Savéant, A. Tallec, R. Tardivel, C. Tardy, J. Am. Chem. Soc. 119 (1997) 2420.
[32] E. Brillas, G. Farnia, M.G. Severin, E. Vianello, Electrochim. Acta 31 (1986) 759.
[33] C. Amatore, M. Gareil, J.-M. Savéant, J. Electroanal. Chem. 147 (1983) 1.
[34] J.-M. Savéant, Elements of Molecular and Biomolecular Electrochemistry. An Electrochemical Approach to Electron Transfer Chemistry, John Wiley & Sons Inc., New Jersey, 2006, p. 154.
[35] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd ed., John Wiley & Sons Inc., New York, 2001, p. 273.