Bulgarian Chemical Communications, Volume 49 Special Issue C (pp. 134– 138) 2017

Electrochemical bond cleavage in pesticide ioxynil. Kinetic analysis by voltammetry and impedance spectroscopy

R. Sokolová[1]*, S. Giannarelli[2,] N. Fanelli[3], L. Pospíšil[1,4]

[1] *J. Heyrovský Institute of Physical Chemistry of the CAS, v.v.i., Dolejškova 3, 18223 Prague, Czech Republic*
[2]*University of Pisa, Department of Chemistry and Industrial Chemistry, via Moruzzi 13, 56124 Pisa, Italy*
[3]*Institute of Chemistry of Organometallic Compounds, CNR Pisa,via Moruzzi 1, 56124 Pisa, Italy*
[4] *Institute of Organic Chemistry and Biochemistry of the CAS, v.v.i., Flemingovo n. 2, 16610 Prague, Czech Republic*

Received October 29, 2016 Revised December 20, 2016

The cleavage of carbon-halogen bond is a common process in electrochemistry of halogenated aromatic compounds. We describe such a cleavage for the reduction of pesticide ioxynil, 4-hydroxy-3,5-diiodobenzonitrile. The reaction mechanism is complicated by the presence of two iodine substituents and by self-protonation equilibrium. We compare three methods for the determination of the rate-determining step. The electrochemical impedance spectroscopy is rarely used for the determination of coupled fast chemical reactions of organic compounds. Our procedure involves simulation of cyclic voltammograms, search for parameters of Gerischer impedance and simulation of the faradaic phase angle as a function of the applied frequency. The last procedure is considerably more sensitive for the detection of chemical reaction compared to fitting the entire electrode impedance spectrum.

Key words: electrochemical impedance spectroscopy, rate constant, self-protonation, faradaic phase angle, halogen cleavage, EC processes fitting

INTRODUCTION

Electron transfer in organic redox systems is often coupled with fast chemical reactions like halogen cleavage. Cyclic voltammetry is usually applied for the determination of the reaction mechanism and corresponding kinetic parameters. The solution of complicated reaction pathways includes several unknown parameters often originating from protonation equilibria. The presence of proton donors influences the number of electrons consumed during the reductive cleavage of halide anions from halogenated aromatic compounds [1-7]. Increased number of "adjustable" parameters leads to ambiguity. The same fitting or simulation results may be achieved with quite different set of kinetic and equilibrium constants.

Ioxynil (Fig. 1) belongs to the group of benzonitrile herbicides which are used in agriculture, because it inhibits the electron transfer in the Photosystem II [8].

The role of self-protonation in the reduction mechanism of ioxynil was studied in dimethylsulfoxide by electrochemical methods (Fig. 2) [9-11]. Final products were identified by GC/MS. The cleavage of the carbon-halogen bond was confirmed also by the detection of iodide anions during electrolysis.

Resulting monohalogenated intermediates are further reduced in the second redox step at more negative potentials.

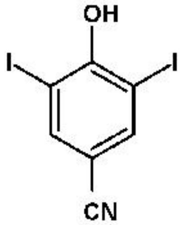

Fig. 1. The chemical structure of ioxynil, 4-hydroxy-3,5-diiodobenzonitrile.

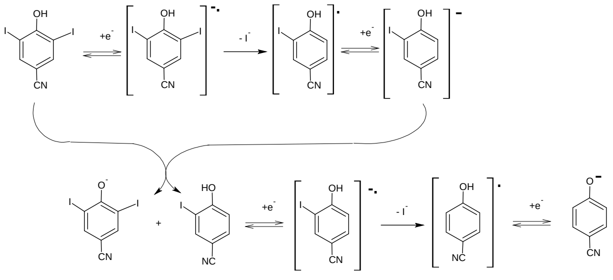

Fig. 2. Mechanism of ioxynil reduction.

Electrochemical impedance spectroscopy (EIS) is a suitable tool for studies of fast processes. However, EIS was rarely applied for analysis of coupled chemical reactions. In this communication we combine established research tools with the application of EIS for the determination of kinetic parameters.

To whom all correspondence should be sent:
E-mail: sokolova@jh-inst.cas.cz

EXPERIMENTAL

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.

Methods

Electrochemical measurements were done using potentiostat Autolab PG STAT 30 equipped with FRA2 module (ECO Chemie, The Netherlands). A three-electrode electrochemical cell was used with an Ag|AgCl|1M LiCl reference electrode (with potential 0.210 V vs. SHE) separated from the test solution by a salt bridge. The working electrode (WE) was a static mercury drop electrode 663 VA Stand (Metrohm) with an area $3.4{\times}10^{-3}$ cm^2. The Stand was interfaced to the potentiostat through controller Autolab IME 663 (ECO Chemie, The Netherlands). The auxiliary electrode was cylindrical platinum net with area ca. 200 times higher than the area of WE. Oxygen was removed from the solution by passing a stream of argon. The electrochemical data from cyclic voltammetry and electrochemical impedance were analyzed and fitted using Autolab software (GPES, FRA). Data were collected in the frequency-scanned mode in the range 0.1 Hz to 100 kHz in both directions. The EIS data were measured on a single mercury drop electrode, which was freshly formed by a trigger pulse and equilibrated for 150 s at a given measurement potential under conditions of stationary state. The prolongation of the equilibration time yielded the same EIS data. Experimental vomtammetric data were fitted by DigiSim software (Version 3.03b, Bioanalytical systems, Inc., USA). Analysis of EIS data used ZView software, version 3.2b (Scribner Associate, Inc., North Carolina, USA). Calculations of the Faradaic phase angle according to Moreira and de Levie [12] treatment were programmed in Mathematica version 8.0 (Wolfram Research, Inc., USA).

RESULTS AND DISCUSSION

Cyclic voltammetry

The cyclic voltammetry of ioxynil shows two reduction peaks at peak potentials -1.0 and -1.4 V (Fig. 3).

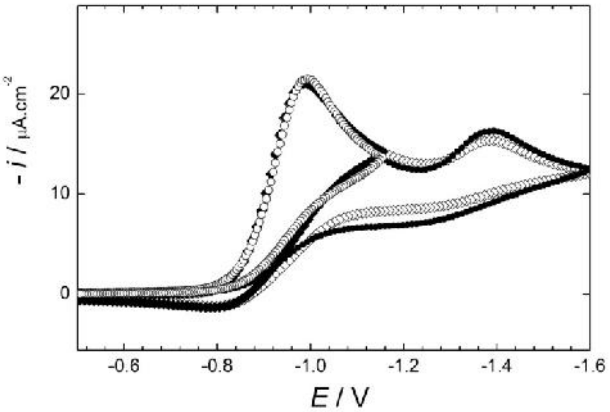

Fig. 3. Cyclic voltammogram of $2.5{\times}10^{-4}$ M ioxynil in dimethylsulfoxide with 0.1 M TBAPF$_6$ supporting electrolyte at 0.2 V·s^{-1}. Experimental data are circles and diamonds are results of the numerical fitting.

Mono-iodinated intermediate is the product of the first reduction peak, in which the reaction mechanism is of ECEC type (E stays for the electron transfer and C for a chemical reaction) [11]. The second reduction peak corresponds to the reduction of mono-iodinated product and the cleavage of the second iodide atom in a sequence of ECE-type process (Fig. 2) [11]. Numerical fitting of voltammograms at scan rates in the range 0.05 to 0.5 V·s^{-1} yielded for the rate determining step $k_1=3.0{\times}10^5$ s^{-1} and K=22. The rate constant of the first iodide atom cleavage is quite high: $k_2 = 7.1{\times}10^8$ s^{-1}. This is in the range of values found for a *single* halogen-carbon bond cleavage in other aromatic systems. Savéant reported the value $1{\times}10^9$ s^{-1} for cleavage of C-halogen bond [13]. M'Halla et al. [7] found rate constants of halogen cleavage $5{\times}10^8$ s^{-1} for 4-chlorobenzonitrile and values $3{\times}10^8$ s^{-1} and $5{\times}10^7$ s^{-1} for 1-bromonaphtalene and 1-chloronaphtalene, respectively.

Electrochemical impedance spectroscopy

The electrochemical impedance data were measured at potentials of the first reduction peak of ioxynil in 50 mV intervals. The measured impedance at the rise of the reduction peak is shown in Figure 4. All data were measured at stationary state and frequencies were scanned in both directions in the interval 0.1 Hz to 100 kHz. No differences were noticed. Data comply with the test based on the Kramers-Kronig transformation [14,15]. An example of EIS data at -0.950 V is shown in Figure 5.

Chemical reactions participating in an overall electron transfer mechanism are known from early studies by DC polarography and later by cyclic voltammetry. The application of AC methods, like EIS, offers measurements on much shorter effective time period. This allows detection of kinetic effects, which in slower techniques would exhibit only thermodynamic influence. Electron transfer reactions coupled with chemical reactions yield the Gerischer-type impedance element (G) [16]. The Gerischer impedance is characterized by an admittance Y_0 and a kinetic parameter $\boldsymbol{k}$ (s^{-1}). The kinetic parameter $\boldsymbol{k}$ is related to the rate constants k_n, k_{-n} and the equilibrium constants $K_n = k_n / k_{-n}$ of the *n*-th's chemical reaction by rather complicated functions [12,17,18]. Due to its complexity, the experimental evidence of the Gerischer-type impedance element was for a long time lacking. First reports were given for systems differing from the present one [19-21]. Hence we explored also a possibility to search for G in electrochemically initiated carbon-halogen bond cleavage.

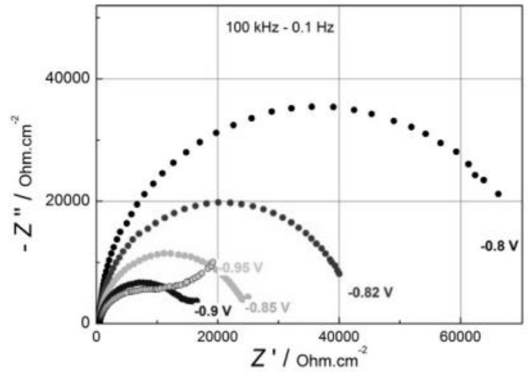

Fig. 4. EIS of 2.5×10-4 M ioxynil in dimethyl-sulfoxide with 0.1 M TBAPF6 supporting electrolyte at potentials indicated at each curve.

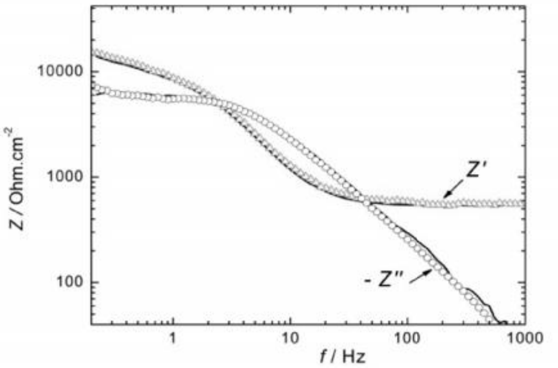

Fig. 5. Experimental impedance data measured at the potential -0.950 V (Z' red points, - Z" black points). The application of the Kramers-Kronig transform yields lines overlapping with experimental points.

The impedance data were fitted using the Randles equivalent circuit and by a similar circuit containing G in place of the Warburg element. Unfortunately the fitting of experimental data could not distinguish which circuit fitted better. The heterogeneous rate constants *k(E)* of the first electron transfer as a function of *E* were estimated from values of the charge transfer resistance[22] and are given in Figure 6.

Knowing from other experiments (cyclic voltammetry, exhaustive electrolysis and product analysis) that chemical steps are indeed involved in the mechanism, heterogeneous rates *k(E)* estimated from the charge transfer resistance R_{ct} are not correct because the Gerischer impedance Z_0 contributes to the overall complex impedance diagram. We estimated Gerischer parameters as $Y_0 = 9.79\times10^{-5}$ S·cm^{-2} and $\boldsymbol{k} \sim 0.195$ s^{-1}. It is known that Z_0 (=1/Y_0) can be detected only for the time-scale of EIS and hence for $10^{-4} < \boldsymbol{k} < 10^{-2}$. Much faster chemical reactions contribute to the overall impedance by Z_0 in the frequency range, where R_{ct} and non-faradaic components prevail. Since experimental data could not be measured for frequencies lower than 0.2 Hz the estimated parameters of the Gerischer impence are not very reliable. Simulation using the fitted parameters Y_0 and $\boldsymbol{k}$ for much lower frequencies outside the measured range is shown in Figure 7. It is evident that data should be measured to much lower frequencies, which is technically impossible for the present system.

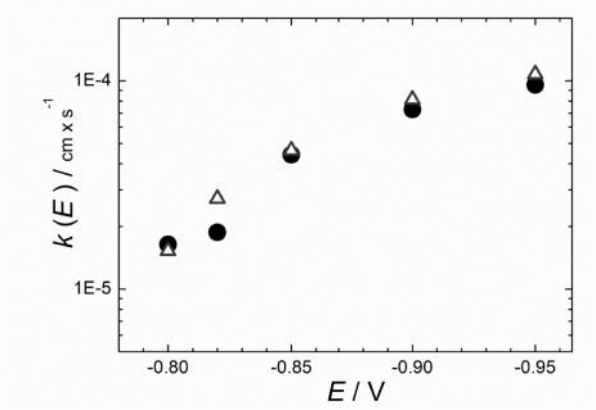

Fig. 6. The heterogeneous rate constant *k(E)* estimated from the charge transfer resistance for two concentrations of ioxynil: (●) 1.9×10^{-4} M and (△) 2.5×10^{-4} M.

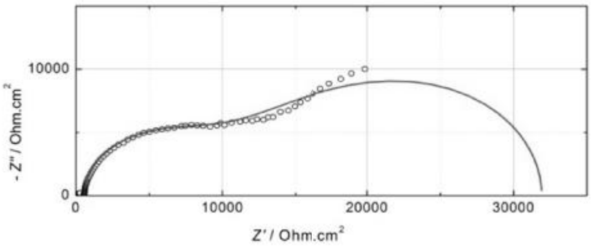

Fig. 7. Diagram of the experimental complex electrode impedance at -0.950 V (circles). Data were fitted with the Gerischer-type circuit resulting in the solution resistance 568 Ohm.cm^{-2}, R_{ct}=8057 Ohm.cm^{-2}, the double layer capacitance 6.23μF.cm^{-2}, Y_0=9.79×.10^{-5} S.cm^{-2} and k = 0.195 s^{-1}. Simulation using these

parameters and the frequency range from 1 mHz to 30 kHz is shown as the red curve.

It was recognized [17] that predicted influence of a chemical reaction is readily apparent from a *qualitative* inspection of the faradaic phase-angle ϕ data, whereas similar examination of impedance vectors diagrams may show no definitive indication of the presence of chemical kinetics. The dependence of the faradaic phase angle on the square root of frequency (cot ¤ *vs.* $\mu^{1/2}$) in such cases shows a hump with low- and high-frequency asymptotes. Our experimental data indeed show such humps of various heights for different DC potentials. An example is given in Figure 8.

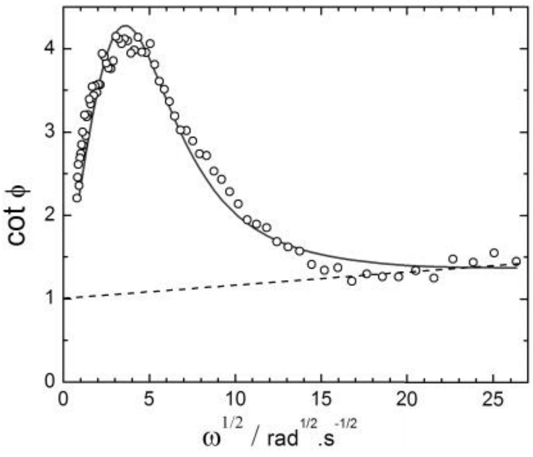

Fig. 8. The experimental dependence of the faradaic phase angle on the applied frequency. The DC potential was -0.95 V. Simulation (full red curve) according to Moreira-De Levie equations used the following values: $k(E)$=0.157 estimated from the dashed asymptote, k_1=76, k_{-1}=3.8, K_1=20.0 and α=0.5.

Simulation of the cot ¤ *vs.* $\mu^{1/2}$ plot yields the rate constants of the chemical rate determining step coupled with the first electron transfer step k_1=3.62×10^5 s^{-1} and K_1=20.0. These data remarkably agree with the corresponding values k_1=3.0×10^5 s^{-1} and K_1=22 obtained by fitting of the cyclic voltammograms.

CONCLUSIONS

The application of three methods for the estimation of the rate determining coupled chemical reaction in electrochemical iodine-carbon bond cleavage was tested. The overall reaction scheme, elucidated in our previous reports, is rather complicated due to the participation of self-protonation process [10,11]. Simulation of cyclic voltammograms was used as an established method in organic electrochemistry. The electrochemical impedance spectroscopy is an alternative for the evaluation of kinetic parameters. However, its application to organic redox systems is lacking. Redox properties of ioxynil indicate that the kinetic Gerischer impedance would be observable in the frequency range, in which also the charge transfer resistance dominates. This makes also the determination of the standard heterogeneous rate constant k^0 quite uncertain (see a non-linear dependence of *k(E) vs. E* in Figure 6). We concluded, as already noticed by Smith [17], that the inspection of the faradaic phase angle as a function of the applied frequency is the most reliable method of proving the coupling of a chemical reaction and the electron transfer. Using the formalism of Moreira and de Levie, we obtained the homogeneous and heterogeneous rate parameters in a good agreement with values estimated from voltammetry. Results reported here promote further attempts to apply EIS for more simple cases of organic EC processes.

Acknowledgements: *This work was supported by the Academy of Sciences of the Czech Republic (RVO: 61388963) and the Grant Agency of the Czech Republic (GACR 14-05180S).*

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ЕЛЕКТРОХИМИЧНО РАЗЦЕПВАНЕ НА ВРЪЗКИТЕ В ПЕСТИЦИДА ЙОКСИНИЛ. КИНЕТИЧЕН АНАЛИЗ С ПОМОЩА НА ВОЛТАММЕТРИЯ И ИМПЕДАНСНА СПЕКТРОСКОПИЯ

Р. Соколова[1], С. Гианнарелли[3], Н. Фанели[4], Л. Поспишил[1,2]

[1] *Чешка Академия на Науките, Институт по физикохимия-Дж.Хеуровску, Долейшкова 3, 18223 Прага, Чехия.*
[2] *Университет в Пиза, Факултет по химия и индустриална химия, Ул. Моруззи 13,56124 Пиза, Италия*
[3] *Институт по химия на органометални съединения, Национален научно-изследователски съвет Пиза,*
ул. Морузи 1, Пиза, Италия
[4] *Чешка Академия на Науките, Институт по органична химия и биохимия, Флемингово 2, 16610 Прага, Чехия*

Постъпила на 29 октомври 2016 г.; коригирана на 20 декември 2016 г.

(Резюме)

Разцепването на връзката въглерод-халоген е обикновен процес в електрохимията на халогенирани ароматни съединения. В тази работа ние описваме такова разцепване при редукция на пестицида йоксинил, 4-хидрокси-3,5-дийодобензонитрил. Механизмът на реакцията е усложнен поради присъствието на два йодни заместителя и на равновесие на самопротониране. Сравнени са три метода за дефиниране на скорост определящия стадий. Електрохимичната импедансна спектроскопия рядко се използва за определяне на сдвоени бързи химични реакции на органични съединения. Нашата процедура включва симулация на циклични волтамограми, търсене на параметрите характерни за импеданса на Геришер и симулация на фазовия ъгъл на фарадеевата реакция като функция на приложената честота. Последната процедура е значително по-чувствителна за откриване на химическата реакция с която трябва да се се направи фитинг на импедансния спектър на електрода.