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Effect of the Electrode Material on the Electrochemical Reduction of Some 2,5-Dihydro-1,3,4-thiadiazoles

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During cyclic voltammetric studies of the 2,5-dihydro-1,3,4-thiadiazoles (Δ^3-1,3,4-thiadiazolines) (**1a**–**e**) on HMDE in 0.1×10^{-3} mol/dm^3 $LiClO_4$ acetonitrile and aqueous-acetonitrile or aqueous-ethanol Britton-Robinson's buffer solutions in second polarization cycle, besides peaks equivalent to polarographic waves, an additional new system of peaks was observed. The corresponding analogous system of additional peaks has not been observed during the reduction of these substances on electrodes of other materials, as *i.e.*, platinum, gold or glassy carbon. This study showed that it results from the oxidation and reduction of organo-mercury compounds, formed in reaction of the electrode material (Hg) with an adsorbed product of 2,5-dihydro-1,3,4-thiadiazoles reduction.

Key words: 2,5-dihydro-1,3,4-thiadiazoles, additional system of redox voltammetric peaks, electrode material effect

Recently [1–3] we noticed some additional system of peaks, observed on the cyclic voltammetric curve describing the second polarization cycle of electrochemical reduction of some 2,5-dihydro-1,3,4-thiadiazoles* solutions using HMDE. The additional peaks were observed at more positive potentials than the respective peak potential of thiadiazole ring reduction and the half-wave potential of polarographic waves. Similar phenomena were also reported by other authors, who reduced electrochemically nitroso-, azoxy- and azo-derivatives [4–6], nitro compounds [6–14] and unsaturated systems containing C=C bond [15]. Appearance of additional peak systems were explained in different manner. The most relevant interpretations are: i) oxidation of electrode reaction products [9–12,14]; ii) oxidation of ionic associates of general formula (AB^{2-}, $2M^+$), where dianion AB^{2-} is an electroreduction product and M^+ is the cation of the supporting electrolyte [13,16]; iii) reaction of the final product of electroreduction with the components of the reaction mixture [4,5,7,8] and iv) reaction with electrode material [6,9]. Diverse aspects concerning appearance of the system of additional peaks during reduction of nitroso-, azoxy- and azobenzene (using HMDE) has extensively been discussed in [6].

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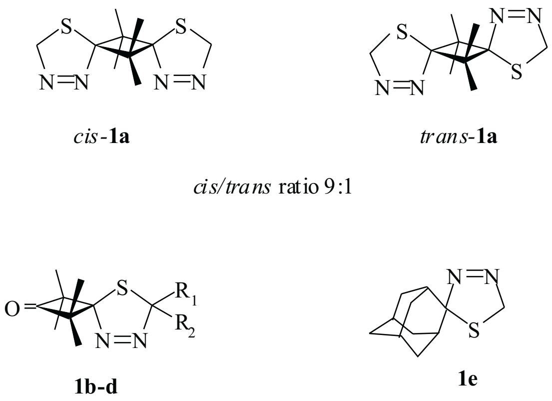
*From now 2,5-dihydro-1,3,4-thiadiazoles will be named according to the traditional nomenclature as Δ^3-1,3,4-thiadiazolines.

In order to determine the conditions responsible for the formation of an additional system of peaks observed during the electrochemical conversions of Δ^3-1,3,4-thiadiazolines [1,2], a comparative study involving a series of differently substituted Δ^3-1,3,4-thiadiazolines (Td) **1a**–**e** has been carried out. Compounds **1** constitute a relatively little known class of five-membered nitrogen-sulphur heterocycles, which are used as precursors of reactive thiocarbonyl ylides or as starting materials in syntheses of 1,3,4-thiazole derivatives [17].

The aim of this study was to explain the relationship between the presence of an additional system of peaks and substitution pattern of the heterocyclic ring, material of the electrode, type of the of solvent and the background electrolyte.

Δ^3-1,3,4-Thiadiazolines included in this study are: an inseparable mixture of *cis* and *trans* isomers (*cis/trans* ratio = *ca*. 9:1) 6,6,12,12-tetramethyl-4,11-dithia-1,2,8,9-tetraazadispiro[4,1,4,1]-dodeca-1,8-diene **1a**; 1,1,3,3-tetra-methyl-8-thia-5,6-diazaspiro-[3,4]oct-5-en-2-on **1b**; 1,1,3,3,7,7-hexamethyl-8-thia-5,6-di-azaspiro[3,4]oct-5-en-2-on **1c**, 1,1,3,3-tetramethyl-7,7-di(*tert*-butyl)-8-thia-5,6-diazaspiro[3,4]-oct-7-en-2-on **1d** and 6,6-tetramethyl-4-thia-1,2-diazadispiro[4,1]-dodeca-1-en **1e**.

Scheme 1



cis-**1a**

trans-**1a**

cis/trans ratio 9:1

1b-d

1e

$R_1 \rangle R_2$ = **b:** H_2 ; **c:** $(CH_3)_2$; **d:** $[(CH_3)_3C]_2$

EXPERIMENTAL

2,5-Dihydro-1,3,4-thiadiazoles (Δ^3-1,3,4-thiadiazolines) **1a**–**e** were prepared following procedure earlier described in [2]. Electrochemical reduction was carried out in acetonitrile in the presence of 0.1×10^{-2} mol/dm^3 $LiClO_4$ and in water-ethanol and water-ethanol buffer solutions in the pH 1.5–11.5. All experimental procedures were identical with those given in [1,3]. The voltammetric curves were recorded in the three-electrode arrangement with a saturated calomel reference electrode and platinum foil counter electrode. A static mercury drop electrode (SMDE 1 Laboratorni Pristroje, CSR) drop area 0.012

cm^2, applied either in the dropping or hanging mode, a glassy carbon electrode of 0.200 cm^2 surface area, gold electrode of surface area 0.015 cm^2 and a platinum electrode of surface area 0.015 cm^2 were used as the working electrodes. The glassy carbon electrode has been cleaned before each measurement by washing in chromic acid solution, then rinsed in triply distilled water and dried using filter paper. The platinum and gold electrodes were polished mechanically with diamond paste and electrochemically in working solutions by cycling the potential over the range near the electrolyte decomposition until a stable voltammogram was obtained [18]. All experiments were carried out at 277± 0.1 K. The solutions were deaerated by using oxygen-free argon.

RESULTS AND DISCUSSION

Examples of cyclic voltammograms obtained for **1a**, **1b**, **1c** and **1d** derivatives in 0.1×10^{-3} mol/dm^3 $LiClO_4$ acetonitrile solutions are given in Figure 1. Test-polarograms and cyclic voltammograms for all compounds **1** in ethanol-water (45% v/v ethanol) containing Britton-Robinson's buffer solutions at pH = 3.6 are presented in Figure 2.

During the second polarization cycle new peaks : cathodic c_3 and anodic a_2 for all **1** on cyclic voltammograms (Figs. 1,2 and 3) in all solvents and solutions studied, except of the bulky substituted derivative **1d** and also cathodic c_4 for **1a**, were observed. Additionally, in the next polarization cycle new anodic peak a_3 (prepeak of a_2) appeared. In contrast to heights, the number of peaks does not change in subsequent polarization cycle. Peaks c_1 and c_2 decreased, while all other increased to approximately the same constant value. This is a clear evidence that products of some electrode processes cumulated on the electrode surface. The voltammetric curves recorded after the positive potential scan direction are similar to those obtained after the third and successive polarization cycles in the negative potential direction.

The potentials of peaks a_2, a_3, c_3 and c_4 were more positive than polarographic half-wave potentials and potentials of peaks c_1 and c_2. On dc polarograms the waves equivalent to these peaks were not observed. The additional peaks a_2, a_3, c_3 and c_4 were observed in the entire pH range and in all solvents applied. The shape and their potentials are nearly identical for all substances. Shapes of additional redox system of peaks and their dependence on experimental variables suggest the occurrence of adsorption phenomena. One can notice that the anodic peak a_2 is much wider than the diffusional one, indicating kinetic character and the cathodic peak c_3 is asymmetric. In Figure 3 there is presented an example of typical changes of additional peak system *versus* the scan rate. Theoretically predicted asymmetry of the peaks for surface processes [18,19] is more outstanding at higher scan rate. In addition, peak currents as a function of the scan rate for peaks a_2 and c_3 indicate the adsorptive character of processes, leading to cathodic c_3 and kinetic to anodic a_2 peaks, respectively.

This hypothesis was confirmed by the peak potential E_p dependence on the log v. At slow sweep rates, the peak potential E_{pc_3} does not depend on the sweep rate. At higher rates, however, the curves show oblique asymptotes with slopes depending on pH: –30 mV, –39 mV and –19 mV at pH = 3.6, 5.8 and 8.1, respectively. It demonstrates that at pH = 8.1 the process is diffusion controlled and takes place on the electrode

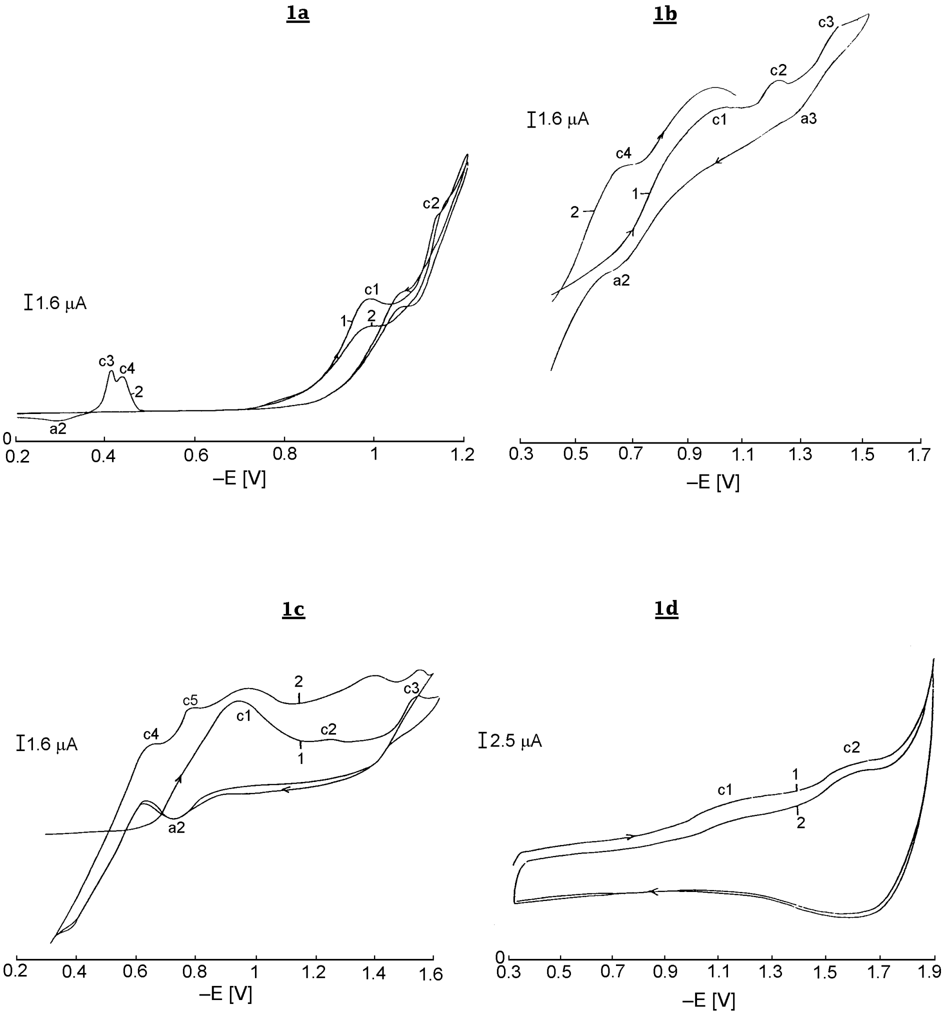


Figure 1. Cyclic voltammograms recorded during the reduction of 3×10^{-4} mol/dm^3 compounds **1a**, **1b**, **1c** and **1d** in 0.1 mol/dm^3 M $LiClO_4$ acetonitrile solutions on HMDE. v = 0.2 V s^{-1}.

surface at pH = 3.6 and 5.8. Potentials of cathodic peak E_{pc_3} at pH 2.2 and anodic peak E_{pa_2} at all pH values are practically independent of the scan rate exhibiting their kinetic character.

At slow sweep rates, the difference between potentials of peaks a_2 and c_3, Δ_{pca}, indicates quasi-reversible 1-electron redox process. At higher sweep rates, however, the difference between potentials of cathodic and anodic peaks increases (Fig. 3).

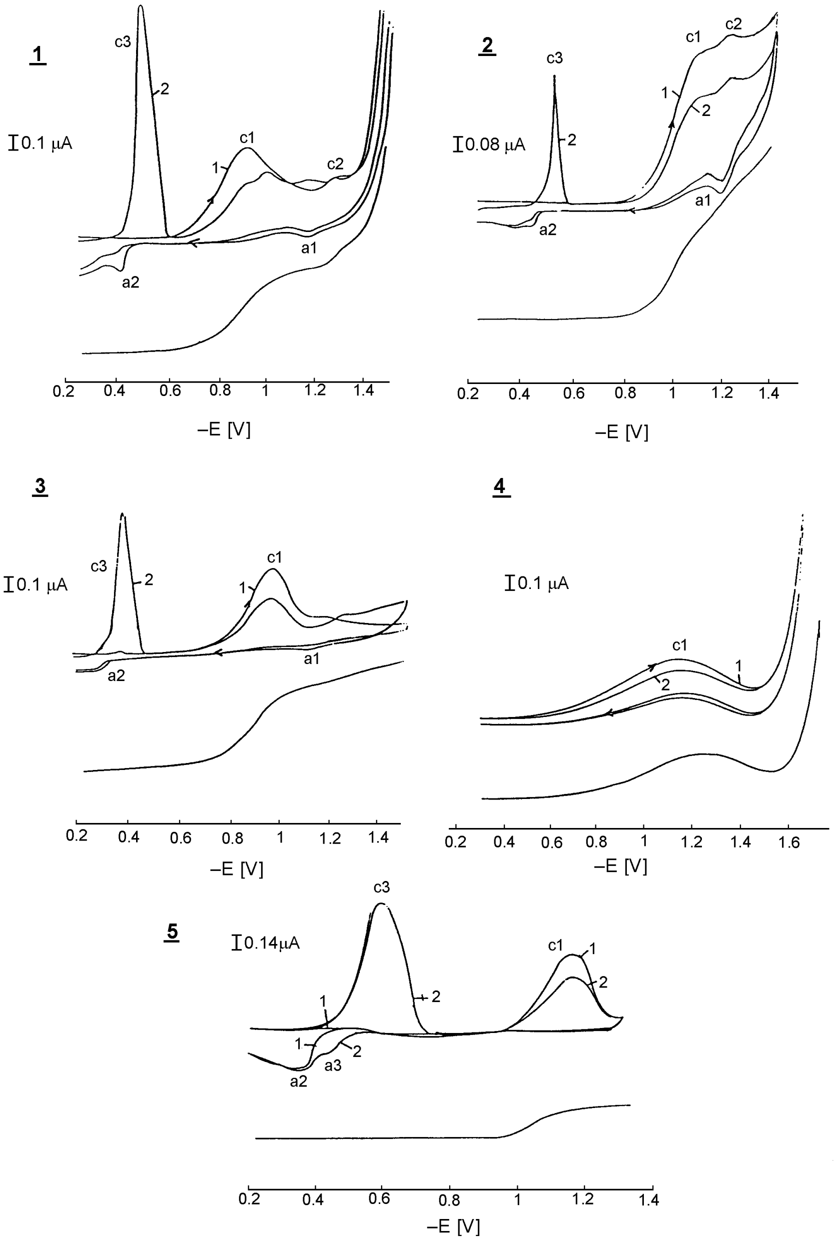


Figure 2. D.c. polarograms and cyclic voltammograms of 1.3×10^{-4} mol/dm^3: 1) **1a**, 2) **1b**, 3) **1c**, 4) **1d** and 5) **1e** in Britton-Robinson buffer solution. pH = 3.60; v = 0.2 V s^{-1}.

It was found for all investigated compounds, that during the polarization of electrodes in different potential ranges, the oxidation reactions occurring at the peaks a_2 and a_3 are conditioned by the reduction reaction corresponding to peak c_1 (*i.e.* Fig. 4, curves 2 and 3). On the other hand, products resulting from the oxidation reaction of

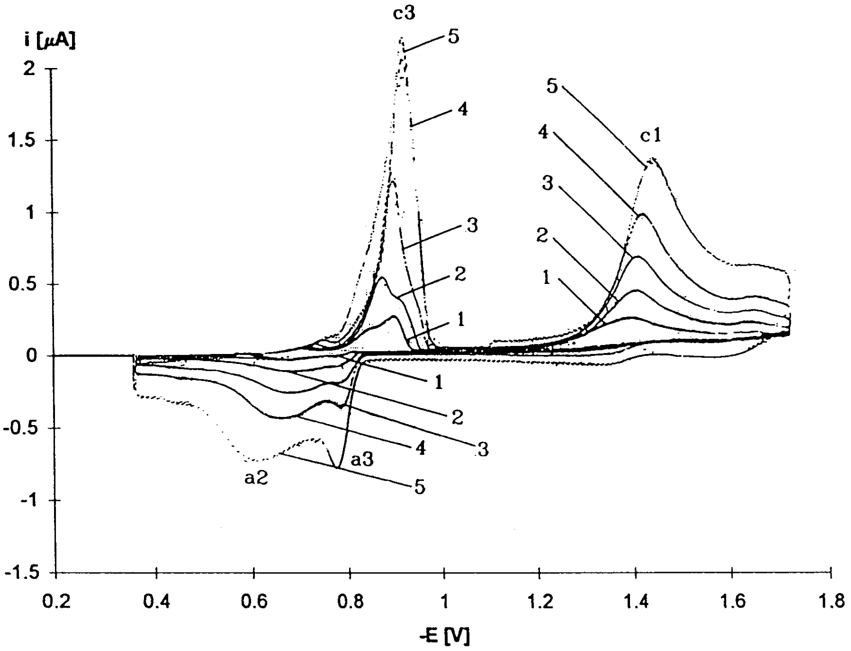


Figure 3. Influence of the scan rate on cyclic voltammograms of 1.3×10^{-4} mol/dm^3 **1e**. Scan rate: (1) 0.02, (2) 0.05, (3) 0.10, (4) 0.20, (5) 0.50 V s^{-1}. pH = 10.22 [1].

peak a_2 are reduced in peak c_3 (Fig. 4 curve 6). Observed phenomenon suggests that the additional system of peaks is associated with an intermediate or the product formed in the course of **1a–c** and **1e** reduction.

On the voltammograms of **1a** in acetonitrile-water solutions two cathodic peaks in the first potential sweep and two additional cathodic peaks c_3 and c_4 in second polarization cycle appeared (Fig. 5). It was found, that peak c_3 is conditioned by the reaction of peak c_1, whereas peak c_4 by the reaction of peak c_2. Earlier [3], we reported that in the case of **1a** electrochemical reactions of peaks c_1 and c_2 are associated with the first and the second N=N bond reduction, respectively. This suggests, that the presence of additional peaks are conditioned by the electroreduction of the N=N bond.

The peak potentials of a_2 and c_3 shift towards more negative values with increasing pH (Fig. 6). This behaviour revealed the preceding protonation reaction. The slope of straight lines indicate a 1 e^-, 1 H^+ reaction and this dependence is in agreement with the result obtained from the difference between anodic and cathodic peaks. The voltammetric dissociation constant of protonated form of products of this transformation is for **1c** $pK'a_c = 9.3$. and $pK'a_a = 8.4$, for **1b** $pK'a_c = 9.1$ and $pK'a_a = 8.0$. For **1a** and **1e** the peak potential did not stabilize with pH-increasing. Example of variations in c_3 and a_2 peak currents for **1c** with pH are shown in Figure 7. The current of peak a_2 is pH-independent, whereas the current of peak c_3 at pH below 8 increases and above this pH value decreases.

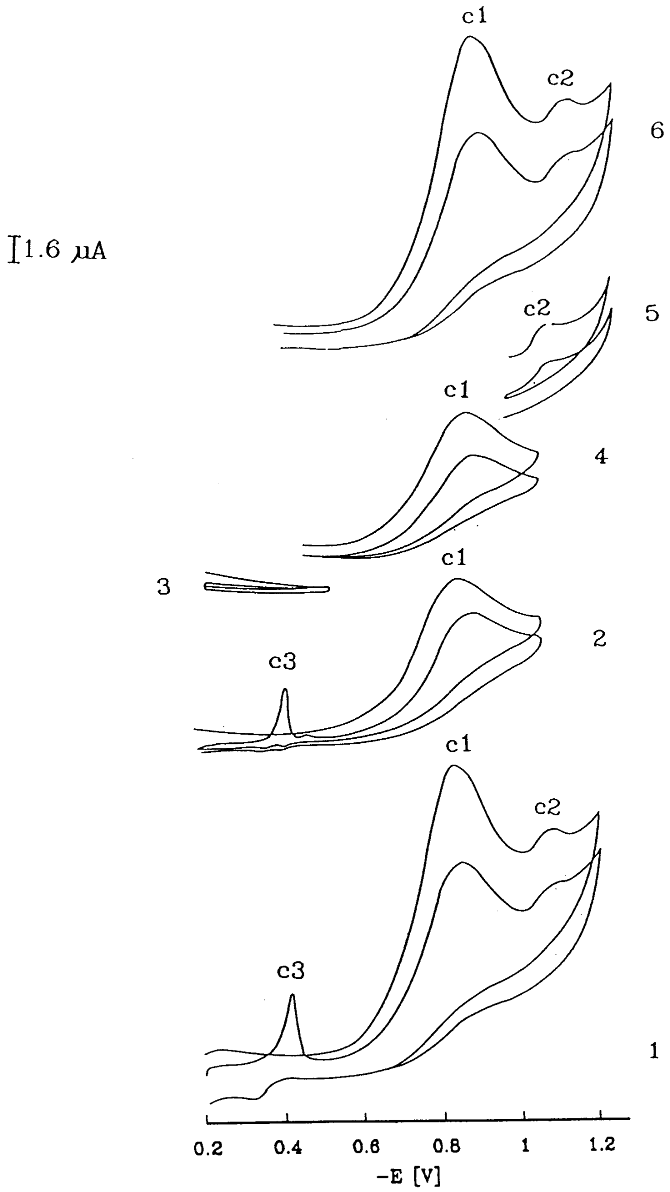


Figure 4. Cyclic voltammograms of 1×10^{-4} mol/dm^3 Th: **1b** in Britton-Robinson buffer pH = 3.6 obtained in different sweep range. Scan rate v = 0.2 V s^{-1}.

Potentials of additional peaks depend also on the nature of the cation of supporting electrolytes. Anodic E_{pa_2} and cathodic E_{pc_3} potentials become more negative with increase of ionic radii of cation, *i.e.* for 1.3×10^{-4} solution of **1c** in the presence of 0.1 mol/dm^3 $NaNO_3$ the peak potential $E_{pc_3} = -0.475$ V, whereas in 0.1 mol/dm^3 KNO_3 $E_{pc_3} = -0.525$ V. The influence of the electrolyte on the processes of additional system

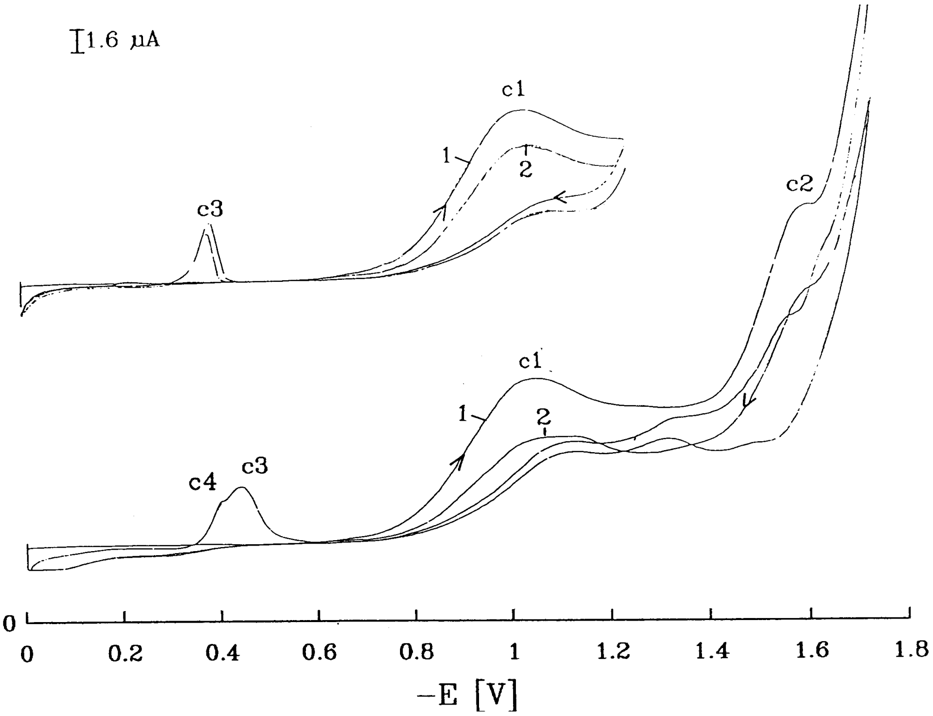


Figure 5. Cyclic voltammogram of 1.3×10^{-3} mol/dm^3 **1a** in acetonitrile-water mixtures (45% v/v). pH = 3.60 (Britton-Robinson buffer solution); sweep range: 1) 0–1.200 and 2) 0–1.800 V; v = 0.2 V s^{-1}.

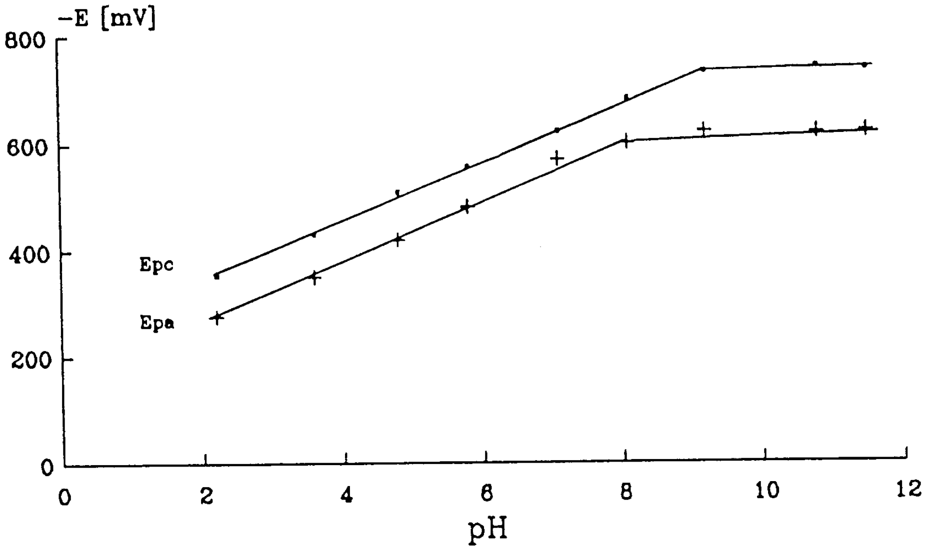


Figure 6. Effect of pH on c_3 and a_2 peak potentials of 1.3×10^{-4} mol/dm^3 **1b** solutions.

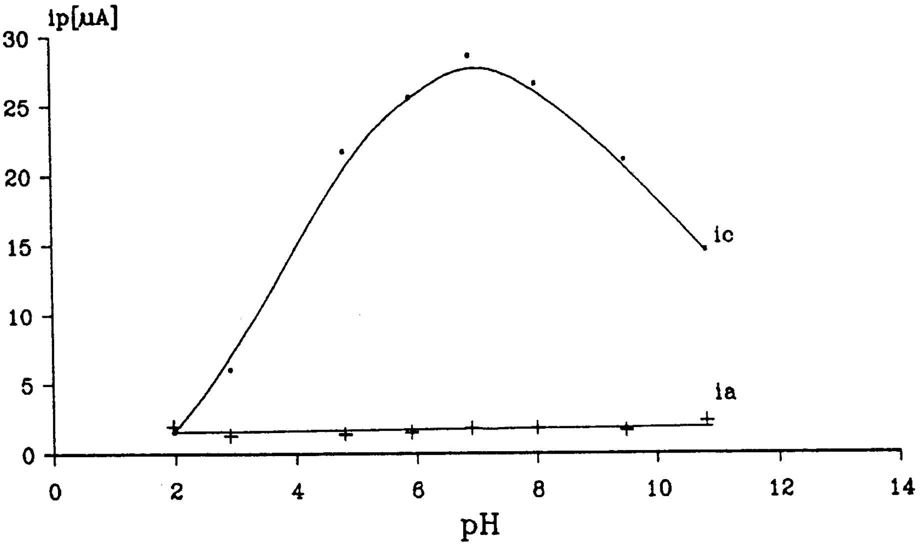


Figure 7. Effect of pH on c_3 and a_2 peak currents of 1.3×10^{-4} mol/dm^3 **1b** solutions.

of peaks is in agreement with previous observations by Kryszczynska, who recorded the additional anodic peak during the electroreduction of azobenzene in DMF [13] and by Lipsztajn *et al.* who reported similar phenomena during electroreduction of nitroso-, azoxy- and azobenzene in DMF at HMDE [6].

Additional system of peaks appears in all solvents used in our studies (*i.e.* in acetonitrile, aqueous-acetonitrile and aqueous-ethanol mixtures), (Figs. 1,2 and 4). The reduction peak c_3 is shifted towards more negative potentials, whereas the oxidation one a_2 towards more positive after replacing ethanol by acetonitrile in mixed solvents. The corresponding values in 1.3×10^{-4} mol/dm^3 **1c** water-ethanol solution (45% v/v ethanol) at pH = 5.3 were $E_{pa_2} = -0.470$ V and $E_{pc_3} = -0.550$ V. In the water-acetonitrile solution (45% v/v acetonitrile) potential values were $E_{pa_2} = -0.420$ V and $E_{pc_3} = -0.630$ V. Potentials were measured *versus* the saturated calomel electrode. However, values of potential difference between the ethanol or the acetonitrile and the water are near the same ($\Delta\varphi_{L(s\leftarrow w)}$ equals for EtOH/water = -0.250 V and for AcN/water = -0.230 V [36,37]) it allows to compare measured data.

It is worth of mentioning, that no additional cathodic peak was observed (Figs. 1 and 2) on voltammmograms of **1d** solutions. By means of IR and NMR spectroscopies we concluded that in the case of **1d**, peaks c_1 and c_2 in aprotic media and c_1 in mixed solvents correspond to the reduction of non-protonated thiadiazole; moreover products were isolated in very small yield [3]. This fact suggests that steric hindrance and strong specific adsorption of depolarizer prevent the preprotonation reaction and

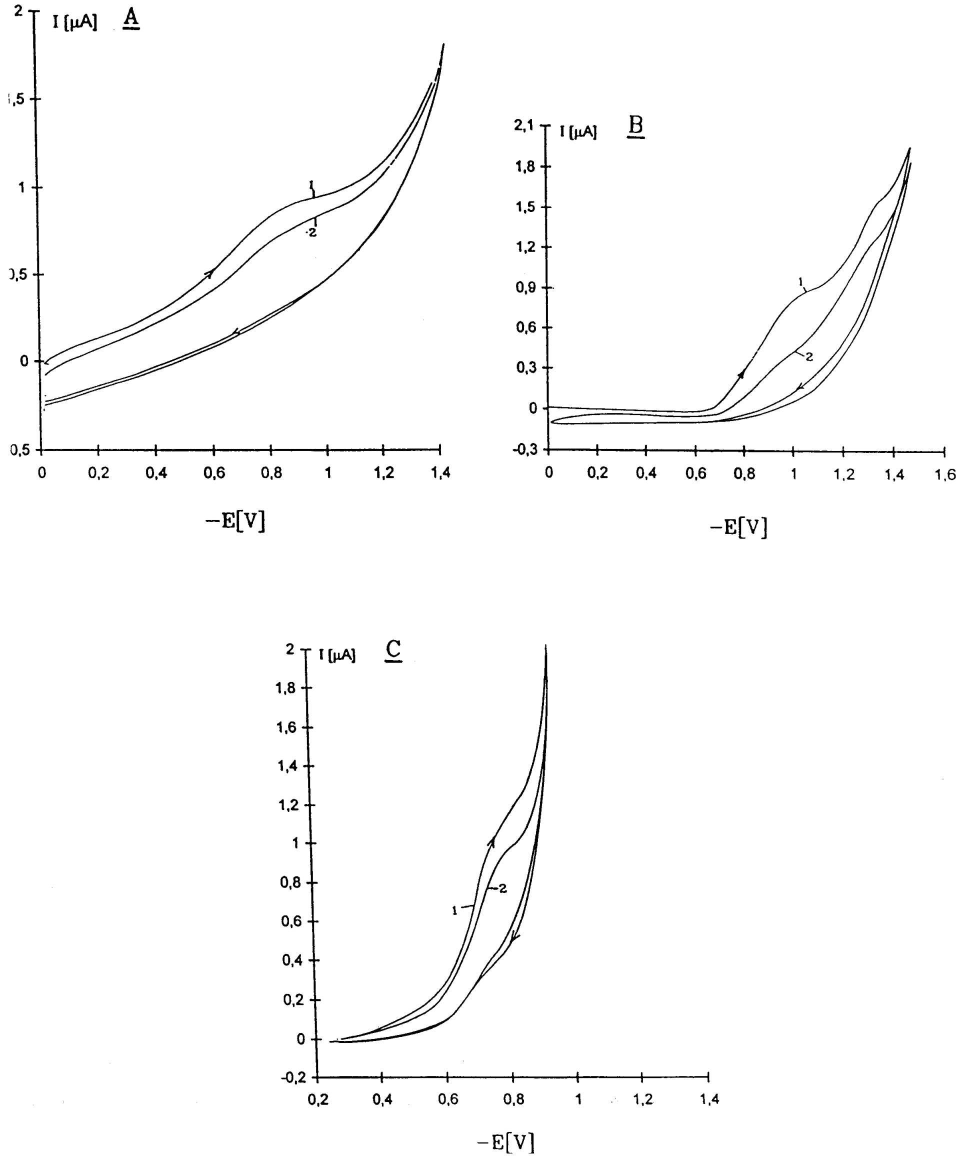


Figure 8. Cyclic voltammogram recorded during the electroreduction of 1.3×10^{-4} mol/dm^3 (A) **1c** at glassy carbon electrode, B) **1b** at a platinum electrode and C) **1e** at a gold electrode. pH = 3.62; v = 0.2 V s^{-1}.

makes the transformation of N=N group more difficult. It supports earlier suggestion, that an additional system of peaks is conditioned by the reduction of N=N bond.

In order to check the influence of electrode material on appearance of additional system of peaks we used also glassy carbon, gold and platinum electrodes instead of

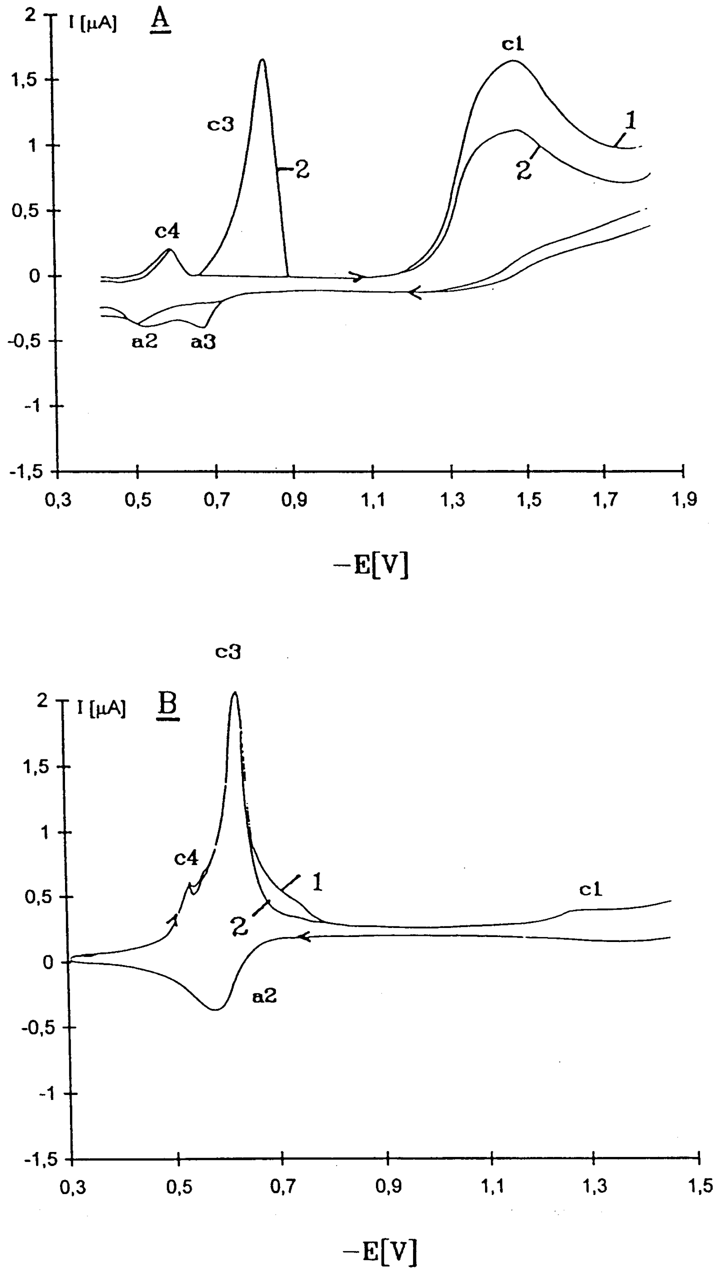


Figure 9. Cyclic voltammogram of 1.3×10^{-4} M Th: A) **1a** and B) **1b** in Britton-Robinson solutions, pH = 11.4; v = 0.2 V s^{-1}.

HMDE. Figure 8 presents typical cyclic voltammetric curves recorded during the reduction of Δ^3-1,3,4-thiadiazolines **1b**, **1c** and **1e** using glassy carbon, platinum and gold electrodes.

In these experiments only bad-formed single cathodic and single anodic peaks (**1e**) and two irreversible (**1c**, **1d**) (glassy carbon electrode), **1c** (platinum electrode) and (**1b**) (gold electrode) or single irreversible cathodic peaks (**1a**, and **1e**) (gold and platinum electrodes) were observed in first and second scans. However, the additional cathodic-anodic system of peaks was not observed. These results indicate a special effect of mercury in electrode processes during the reduction of Δ^3-1,3,4-thiadiazolines and its responsibility for the appearance of the additional peak system.

Base induced ring opening of Δ^3-1,3,4-thiadiazolines, resulting in formation of ring opened species containing thiol function, was already reported [21,22]. We suggest that similar ring opening can lead to formation of an electroactive mercury salt. Similar reactions of substances with thiol functional group on mercury electrodes were described by many authors [23–28]. The opening of heterocyclic ring was observed in alkaline solutions using only derivatives **1a**, **1b** and **1e** containing hydrogen atoms at C-2 [2,3]. Therefore, this reaction cannot be connected with the appearing of an additional redox system (peaks a_2, c_3 and c_4) but it could cause deformation of peak c_3 by new peak c_6 observed in alkaline solutions during the reduction of corresponding **1** [1,3]. This suggestion is supported by new quasi-reversible polarographic waves observed for **1a** and **1b** in alkaline solutions (pH >10) at potentials close to those of a_4 and c_5 peaks (Fig. 9).

All these facts allow us to conclude, that a special role must be attributed to an interaction of mercury with the adsorbed product of the electrochemical reduction of N=N bond in thiadiazole ring.

In [1,3] three types of the mechanism of Δ^3-1,3,4-thiadiazolines (Td) reduction on mercury electrodes in aprotic, acidic and neutral media, were proposed:

– type, in which protonated form TdH^+ undergoes subsequent irreversible reduction:

$$Td + H^+ \leftrightarrow TdH^+ + e \longrightarrow TdH^{\bullet} + e \longrightarrow TdH^- + H^+ \leftrightarrow TdH_2 \quad (1)$$

– type, when the protonation of molecules takes place prior to the first electron transfer:

$$Td + H^+ \underset{k_b}{\overset{k_f = f(pH)}{\leftrightarrow}} TdH^+ + e \longrightarrow TdH^{\bullet} + e \leftrightarrow TdH^- + H^+ \leftrightarrow TdH_2 \quad (2)$$

– type, in which the electrochemical reduction of thiadiazoles could occur in two step processes

$$Td + e \longrightarrow Td^{\bullet -} + e \longrightarrow Td^{2-} \quad (3)$$

In solution of $pH < 8$ both processes (1) and (2) could occur in parallel. However, when $pH > 8$ and in aprotic media only mechanism given by (3) can be taken into account [1,3].

We considered two possibilities of formation of additional peaks. One of them is based on assumption of an interaction of mercury with the radical $TdH^{\bullet}$ ($Td^{\bullet}$) formed during the thiadiazoline ring reduction on mercury electrode. This reaction affords producing an organo-mercury compound of type Td-Hg-Td. Formation of similar compounds on the surface of Hg-cathode during electrolysis of some organic depolarizers has previously been reported [6,13,29–32]. Second possibility is oxidation and reduction of mercury in the presence of the TdH^{-} or Td^{2-} anions, similarly to Lipsztajn *et al.* suggestion [6]. Thus, the following reaction could be formulated:

$$(Td^{2-}, 2\,M^{+})_{ads} + Hg - 2\,e^{-} \longleftrightarrow (Td^{2-}, Hg^{2+})_{ppte} + 2\,M^{+} \qquad (4)$$

where M^{+} is the cation of the supporting electrolyte. On the basis of presented experimental results and some other observations, described in [1,3,33–35], the second hypothesis seems to be most justified for the following reasons: i) Only anions are formed in all solutions used. ii) Radicals $TdH^{\bullet}$ are rather unstable and during the reduction of N=N bond in aqueous-organic solvents only one peak is observed. Two peaks observed for **1b** correspond to protonated and non-protonated form of N=N bonds. For **1a** two peaks are connected with reduction of two N=N bonds which exist in this derivative [3]. iii) In protolytic solvents the reduction peak potential is pH-dependent. At $pH < 8$ reduction potentials become more negative as the pH increases. It indicates that the electrode reactions are preceded by the protonation of reactant and that the rate-determining step (rds) is this reaction. Hence, at higher pH an increasing slowness of the preprotonation reaction took place. However, this same argument could be used in first idea about interaction between mercury and radicals. iv) Variations in c_3 and a_2 peak currents with pH are characteristic (Fig. 7). The current of peak a_2 is pH-independent and has a kinetic character, whereas the current of peak c_3 at pH below 8 increases and above this pH value decreases. The same dependences are obtained for other compounds **1**. This result suggests, that below pH 8 the concentration of anion increases with increasing pH according to (1) and (2), however, at higher pH values a strong adsorption of OH^{-} ions caused the desorption of adsorbed thiadiazole anions from electrode surface. v) Voltammograms recorded during the repeated scans indicated an accumulation of the reaction product at electrode surface (the decrease of peaks c_1 and an increase of peaks a_2 and c_3). The shape of additional peaks suggests a strong adsorption of product (anodic prepeak a_3) and substrate (asymmetrical, sharp cathodic peak c_3). vi) Dependence of potentials of the additional peak system on the nature of cations and on the type of solvent can be explained by the influence of these factors on the solubility of product considered as an organo-mercury compound as suggested in [6]. vii) After long-time electrolysis of **1** carried out at the potential of reduction peak c_1 no additional peak system is observed on voltammograms and a small amount of precipitate is formed. In addition, small drops of mercury appeared at the surface of the electrode.

Obtained results confirm the hypothesis which emphasises the important role of electrode material in electrochemical reactions of organic compounds as underlined in [6,9,32].

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REFERENCES

1. Turowska M., Mlostoń G. and Raczak J., *Polish J. Chem.*, **67**, 1105 (1993).
2. Turowska M., Mlostoń G., Romański J. and Raczak J., *Collect. Czech. Chem. Commun.*, **63**, 31 (1998).
3. Turowska M., Mlostoń G., Celeda M. and Raczak J., *Polish J. Chem.*, **76**, 839 (2002).
4. Lipsztajn M., Krygowski T.M., Laren E. and Galus Z., *J. Electroanal. Chem.*, **57**, 339 (1974).
5. Lipsztajn M., Krygowski T.M., Laren E. and Galus Z., *J. Electroanal. Chem.*, **54**, 313 (1974).
6. Lipsztajn M., Krygowski T.M. and Galus Z., *J. Electroanal. Chem.*, **81**, 347 (1977).
7. Kemula W. and Sioda R., *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **10**, 107 (1962).
8. Krygowski T.M., Stencel M. and Galus Z., *J. Electroanal. Chem.*, **39**, 395 (1972).
9. Kemula W. and Zawadowska J., *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **23**, 275 (1975).
10. Greig W.N. and Rogers J.W., *J. Am. Chem. Soc.*, **91**, 5495 (1969).
11. Rogers J.W. and Watson W.H., *Anal. Chim. Acta*, **54**, 41 (1971).
12. Farnia G., Mengoli G. and Vianello E., *J. Electroanal. Chem.*, **50**, 73 (1974).
13. Kryszczynska H., Ph.D. Thesis, Institute of Chemistry, University of Warsaw, 1974.
14. Sadler J.L. and Bard A.J., *J. Am. Chem. Soc.*, **90**, 1979 (1968).
15. Stengle J.Z. and Peters D.G., *J. Electroanal. Chem.*, **286**, 89 (1990).
16. Avaca K.L.A. and Bewich A., *ibid.*, **41**, 405 (1973).
17. Huisgen R. and Mlostoń G., *Tetrahedron Lett.*, **26**, 1049 (1985).
18. Piela B. and Wrona P.K., *J. Electroanal. Chem.*, **388**, 69 (1995).
19. Hulbert M.H. and Shain I., *Anal. Chem.*, **42**, 1049 (1970).
20. Laviron E., *J. Electroanal. Chem.*, **52**, 355 (1974).
21. Mlostoń G. and Huisgen R., *Tetrahedron Lett.*, **26**, 1053 (1985).
22. Mlostoń G., Romański J., Linden A. and Heimgartner H., *Helv. Chim. Acta*, **80**, 230 (1997).
23. Stricks W. and Kolthoff J.M., *J. Am. Chem. Soc.*, **75**, 5673 (1953).
24. Stankovich M.T. and Bard J.A., *J. Electroanal. Chem.*, **75**, 487 (1977).
25. Moore W.M. and Gaylor V.F., *Anal. Chem.*, **49**, 1387 (1977).
26. Brown E.R. and Sandifer J.R., *Physical methods of Chemistry. VII. Electrochemical methods*. Wiley. Interscience. NY 1986, p. 301.
27. Costa Garcia A. and Tunon Blanco P., *J. Electroanal. Chem.*, **245**, 157 (1988).
28. Karpinski Z.J., Karny M. and Kublik Z., *J. Electroanal. Chem.*, **288**, 129 (1990).
29. Tafel J., *Ber.*, **39**, 3626 (1906).
30. Koch J.K., *J. Am. Chem. Soc.*, **77**, 3208 (1955).
31. Tomilov A.P. and Brago I.N., in Frumkin A.N. and Ershler A.B. (Eds.), *Progress in Electrochemistry of Organic Compounds*, Vol. 1, Plenum Press, London 1971.
32. Tallec A., *Electrochimie Organique*, Masson, Paris 1985, p. 25, 162.
33. Kashin A.N., Ershler A.B., Strelets V.V., Butin K.P., Beletskaya I.P. and Reutov O.A., *J. Organometal. Chem.*, **39**, 237 (1972).
34. Kolthoff J.M. and Barnum C., *J. Am. Chem. Soc.*, **62**, 3061 (1940).
35. Butin K.P., Strelets V.V., Kashin A.N., Beletskaya I.P. and Reutov O.A., *J. Organometal. Chem.*, **64**, 181 (1974).
36. Trasatti S., *J. Chem. Soc. Faraday Soc.*, **170**, 1752 (1974).
37. Scholl H., *Solvation and Electrochemical Processes in Nonaqueous Solvents*. (in Polish). Publishers of University of Łódź, Poland, 1992, p. 190, Tabl. 6.2.