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Study of Electrochemical Behaviour of Some 2,5-Dihydro-1,3,4-thiadiazoles

by M. Turowska[1]*, G. Mlostoń[2], M. Celeda[2] and J. Raczak[1]

[1]*Department of General and Inorganic Chemistry*, [2]*Department of Organic and Applied Chemistry*
University of Łódź, ul. Narutowicza 68, 90-136 Łódź, Poland

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Polarographic, linear-sweep cyclic voltammetric and coulometric at controlled potential studies of some 2,5-dihydro-1,3,4-thiadiazoles (Δ^3-1,3,4-thiadiazolines) on mercury electrodes have been performed in acetonitrile over pH range 1.2–13 in water-ethanol and water-acetonitrile mixtures with Britton-Robinson's buffer. Under conditions of present study, thiadiazoles are reduced to respective thiadiazolidines, and the N=N bond is reduced faster than the C=O group. All electrochemical reactions at pH < 7 are pH dependent and at pH > 7 influenced by surface characteristics. Electrode reaction mechanisms are presented and discussed.

Key words: 2,5-dihydro-1,3,4-thiadiazoles (Δ^3-1,3,4-thiadiazolines), electrochemical study, structural effect

2,5-Dihydro-1,3,4-thiadiazoles of type **1** are versatile materials for syntheses of sulfur-containing systems. In thermal reactions, under mild conditions (40–50°C) they extrude nitrogen to generate reactive thiocarbonyl ylides [1–3] intercepted by electrodeficient dipolarophiles and nucleophilic reagents with general formula RxH (x = O, S). In addition, they are interesting systems for electrochemical studies, since they contain divalent sulfur atom and an isolated N=N azo-moiety incorporated into heterocyclic ring. Aromatic thiadiazoles and oxadiazoles were frequently explored in polarographic studies [4–8], but electrochemical behaviour of their hydrogenated analogues has not previously been studied. In several papers electrochemical studies with open-chain azo-compounds were reported [9–18], however, there are only few studies, which involve electrochemical conversions of cyclic compounds containing N=N double bond as a part of a cyclic system [18–20].

In an earlier study, Huisgen and Mloston reported that 2,5-dihydro-1,3,4-thiadiazoles showed a strong influence of substitution pattern on the rate of nitrogen elimination [21,22]. As a continuation of our systematic studies on the electrochemistry of 2,5-dihydro-1,3,4-thiadiazoles [23], we present in this paper our recent results on the influence of substituents pattern at C-2 on their electrochemical properties. The aim of the present study was to establish effect of substitution on the polarographic and voltammetric behaviour of thiadiazoles **1a–1d** and to compare obtained results with corresponding studies described earlier for spiro-adamantane derivative **1e** [23].

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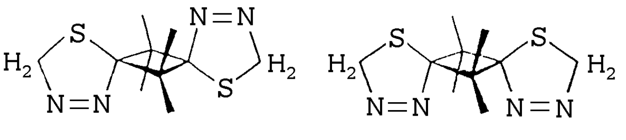
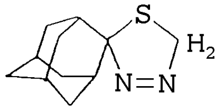
*Author to whom correspondence should be addressed.

Compounds involved in the present study are following:

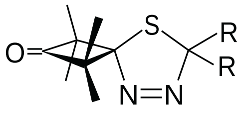
Scheme 1



cis/trans **1a**



1e



1b–d

1	R
b	H
c	CH_3
d	$(CH_3)_3C$

EXPERIMENTAL

2,5-Dihydro-1,3,4-thiadiazoles (Δ^3-1,3,4-thiadiazolines) **1a-d** were synthesized from 2,2,4,4-tetramethylcyclobutanedithione (dithione) or 2,2,4,4-tetramethyl-3-thioxocyclobutanone (monothione) according to known procedures by treatment with corresponding diazocompounds. The following products were obtained: a mixture of *cis/trans*-6,6,12,12-tetramethyl-4,11-dithia-1,2,8,9-tetraazadispiro-[4,1,4,1]-dodeca-1,8-diene **1a** [24]; 1,1,3,3-tetramethyl-8-thia-5,6-diazaspiro[3,4]oct-5-en-2-one **1b** [3]; 1,1,3,3,7,7-hexamethyl-8-thia-5,6-diazaspiro[3,4]oct-5-en-2-one **1c** from monothione and 2-diazopropane [25] and 1,1,3,3-tetramethyl-7,7-di(*tert*-butyl)-8-thia-5,6-diazaspiro[3,4]-oct-7-en-2-one **1d** from monothione and di(*tert*-butyl)diazomethane [26]. Compound **1a** was isolated as an inseparable mixture of *cis* and *trans* isomers (*cis/trans* ratio = *ca.* 9:1). The structure of each of the isolated compounds was confirmed spectroscopically and by elemental analysis.

Thiadiazoline stock solutions were prepared by dissolving the weighed samples in acetonitrile or mixtures of acetonitrile or ethanol with triply distilled water. All reagents used in this study were of high purity.

The measurements in water-acetonitrile and water-ethanol solutions were carried out at controlled pH by using Britton-Robinson's buffers and acetate buffers. The pH values were examined using a N-512 pH-meter (Mera-Elwro, Poland). The requisite readings for water-ethanol solutions were corrected according to [27,28]. pH values of water-acetonitrile solutions were examined before the acetonitrile addition.

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 and controlled life-time t = 4 s was applied either in the dropping or hanging mode.

All experiments were performed by using a PPW-1 Polarograph (Elpan, Poland), which was connected with an X-Y recorder. Coulometer, TYPE QM-3 (ASP Łódź, Poland), was used for coulometry at a controlled potential. The UV-VIS and IR spectra were recorded with Specord UV-VIS spectrophotometer and Specord 71 IR spectrometer (Carl Zeiss, Jena, Germany), respectively.

All experiments were carried out at 277 ± 0.1 K to avoid thermal decomposition of 2,5-dihydro-1,3,4-thiadiazoles. All solutions were deaerated by using oxygen-free argon.

RESULTS AND DISCUSSION

It is useful to divide the studied compounds into two groups, depending upon whether they have one or two types of electroactive groups, *i.e.* (i) containing only azo groups (compound **1a**) and (ii) containing both, azo and carbonyl groups (compounds **1b**, **c** and **d**). Both groups are expected to be reducible on mercury electrodes [15,16].

Derivative **1a** belongs to the first group since it possesses N=N bond in each thiadiazole ring. Solutions of **1a** in acetonitrile display two reduction peaks in first polarization cycle at potential near each to other (Fig. 1 A). The heights of peaks and their ratio were dependent on the polarization rate. At slow scan-rates the second peak is higher than first one, in contrast to the high rate. However, after the addition of water four peaks were observed (Fig. 1B). It suggests that two new peaks at more positive potential correspond to electroconversion of protonated forms of **1a**. In water-ethanol buffer solutions at pH < 3 one reduction voltammetric peak and one polarographic wave were observed, however, at 3 < pH < 6 two dc polarography waves or two reduction voltammetric peaks, which overlapped into one wave or one peak in solutions at higher pH, were recorded (Fig. 2).

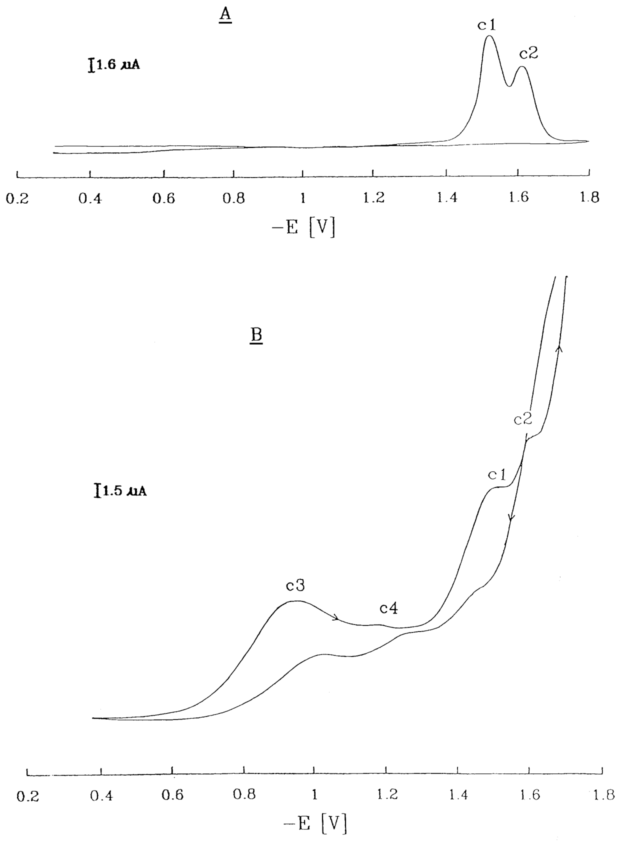


Figure 1. Cyclic voltammograms of 1×10^{-4} M **1a**: A) in acetonitrile 0.1 M $LiClO_4$ solution and B) in acetonitrile-water (45% v/v) 0.1 M $LiClO_4$ solution. Scan rate 200 mV/s.

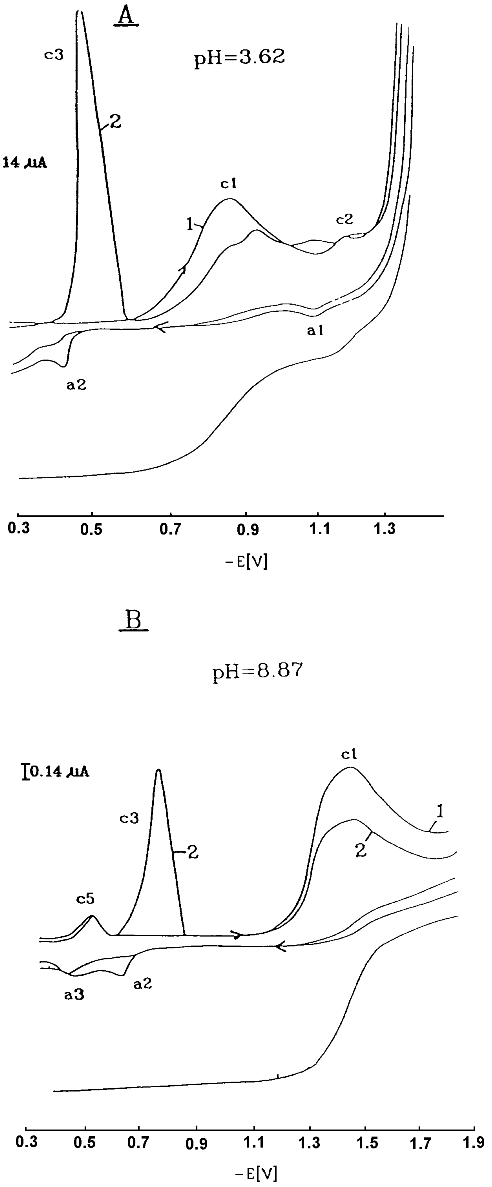


Figure 2. Variation of dc polarograms and cyclic voltammograms recorded during the reduction of 1×10^{-4} M **1a** in Britton-Robinson's buffers at pH values: A) 3.62 and B) 8.87. (1) first cycle and (2) second cycle. Sweep rate 200 mV/s.

The results obtained from the coulometric experiment at pH = 3.62 and E = –1.3 V, at pH = 9.0 and E = –1.7 V in water-ethanol solutions and at E = –1.6. V in acetonitrile indicate that in the case of **1a** the overall number of electrons involved in the electrochemical reduction is *ca.* four electrons in acidic, basic and aprotic (acetonitrile) solutions. This was confirmed by comparing the dc polarogram of **1a** thiadiazole at pH 5.4

with that corresponding to isonicotinamide at pH 4, for which the number of electrons exchanged is four [17]. This result suggests that both N=N group could be reduced or that the reduction process could proceed *via* a mechanism involving successive reduction of one N=N bond with concomitant cleavage of the double bond. However, this second possibility is excluded because the reduction process at more negative potential is quasi-reversible in buffer solutions at $3 < pH < 6$ (peaks: c_2–a_1). Cleavage of the N=N bond was reported by Lund to accompany polarographic reduction of 3,3-pentamethylenediazirine [18].

The ratio of the height of both polarographic waves and voltammetric currents of peaks c_1 and c_2 of thiadiazole **1a** reduction changes with pH and with the scan rate. This conclusion indicates that the electrode reactions of peaks c_1 and c_2 cannot correspond to the reduction of either *cis* or *trans* isomers of compound **1a**, because the equilibrium between these two forms is pH-independent.

In the presence of an acid, tautomerization of Δ^3-thiadiazoline to the corresponding Δ^2-isomer may be expected. In fact, the ^{1}H-NMR study in $CDCl_3$ solutions of the adamantane derivative of Δ^3-1,3,4-thiadiazoline containing a catalytic amount of trifluoroacetic acid indicated that a slow isomerization occurred. However, isomerization was complete only after 3 weeks when the temperature of the sample was maintained at 4°C [24]. For this reason, we assumed the absence of Δ^2-isomer when $pH < 8$, because all solutions were freshly prepared and immediately used in the study.

It was established by conventional methods, that limiting polarographic currents of the first wave and of the c_1 peak at low concentration and in acidic solutions are diffusion controlled and in neutral or basic solutions have adsorptive character, whereas second wave and reduction peak c_2 currents show a kinetic character.

The occurrence of the surface process, that parallels the heterogeneous reaction, can result in increase of the apparent reversibility [29]. The quasi-reversible system of **1a** observed at more negative potential (*i.e.*, peaks: c_2–a_1 in buffer solutions) can be attributed to these phenomena.

It results from the pH-dependence of the potentials ($E_{1/2}$, E_p), and of the currents (i_l, i_p) of electrode processes of **1a** (Fig. 3) that in acidic and neutral solutions acid-base equilibrium are concomitant with charge transfer and are involved in the electrolysis mechanism of **1a** [30,31,32]. In basic media, however, wave heights and peak currents are pH-independent, what indicates that the electroactive species are not protonated in solutions [33]. These results suggest that both protonated and nonprotonated forms of **1a** are electroactive.

Experimental values of the slopes of plots of $E_{1/2}$ and E_p *vs.* pH (Fig. 3) are 55 mV (pH unit)$^{-1}$ for peak c_1 at $pH < 3.5$ and for peak c_2 at all pH used, and 110 mV (pH unit)$^{-1}$ for peak c_1 above pH 3.5. This is in agreement with results of the logarithmic analysis of the dc waves of **1a** made in the form $\log[(I_l-I)/I]$ *vs.* E, where I_l is the limiting current, at different pH. Slopes of the asymptotes are about 120 and about 55 mV per log unit, respectively. According [30], the slope value, *ca.* 120 mV (pH unit)$^{-1}$, corresponds for an irreversible electrode process, in which reduction started by a

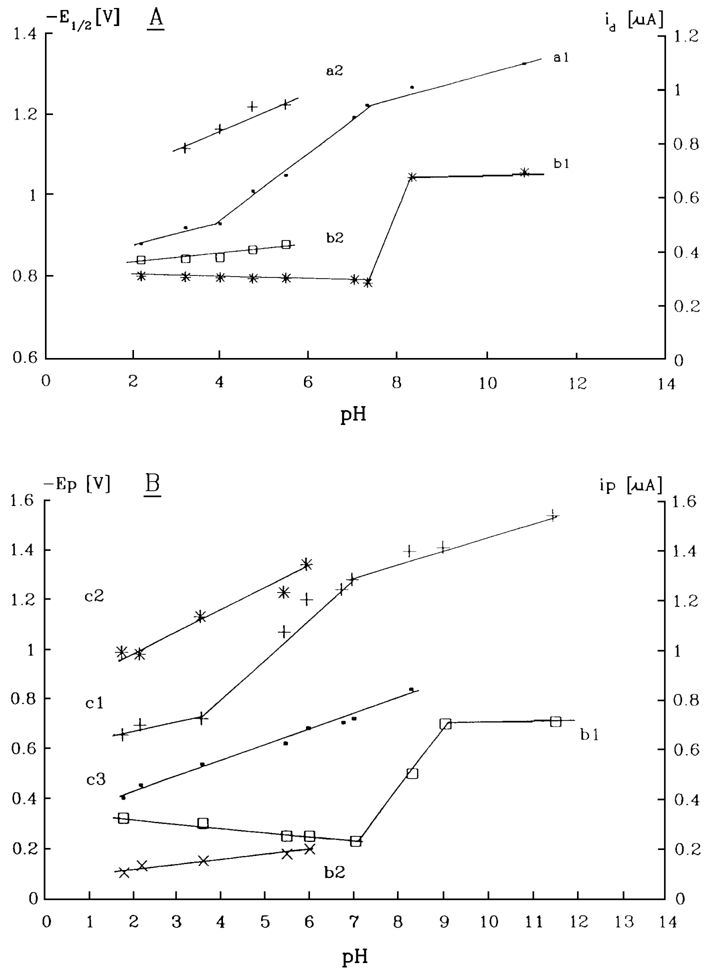


Figure 3. Effect of pH on: A) half-wave potentials $E_{1/2}$ (a_1) and (a_2) and limiting currents i_l (b_1) and (b_2) of first and second waves and B) peak potentials E_p (a_1), (a_2) and (a_3) and peak currents i_p (b_1), (b_2) and (b_3) of c_1, c_2 and c_3 peaks, respectively, for 1×10^{-4} M **1a** in Britton-Robinson's buffers.

reversible electron transfer, followed by a slow protonation process [30, eq. 5.1.1.2]. The slope value, *ca.* 55 mV per pH unit indicates an irreversible electrode process, in which the protonation of reactant takes place prior to the first electron transfer. In the pH range over which the limiting current decreases, the process is partially controlled by the preceding protonation reaction [30, eq. 4.1.2.1]. Heyrovský and Vavřicka [30] elaboration of the theoretical relation for the pH-dependence of the half-wave potential of irreversible reduction the surface processes has not been taken into account. As was reported above in our work the current at low concentrations has diffusion character. For this reason we made also experiments at low reactant concentrations, in which the effect of adsorption can be neglected. Results obtained are very similar to those for higher concentrations.

As mentioned above, the overall number of electrons involved in the electrochemical reduction of **1a** is *ca*. four electrons in acidic, basic and aprotic (acetonitrile) solution. Reaction orders with respect to the H^+ ion concentration calculated according to equation $(\delta \log i/\delta \log [H^+])_E$ were as follow: 1.8 (peak c_1), 1.6 (peak c_2) at $pH < 7$ and 0 at $pH > 8$. These results suggest that both N=N groups of **1a** are reduced according to the similar ways giving one wave or one peak for each type of the mechanism.

Results of MNDO calculations for thiadiazole **1a** indicate that protonation of nitrogen atoms should occur in this derivative relatively easily. However, this process occurs only at one nitrogen atom in each ring. The apparent dissociation constants of both protonated N=N bonds, obtained with the potentiometric method, are very similar, *i.e.*, $\log Ka_1 = 3.19$ and $\log Ka_2 = 3.47$, respectively [34]. The very small difference between the rate of the protonation reaction of species should not influence on the type of electrode reaction. Therefore, one wave or one peak observed during electroreduction of both protonated and nonprotonated species may result from the symmetry of the molecular structure of **1a**.

At pH > 8, **1a** exists predominantly in the nonprotonated azo-form and under these conditions a single reduction wave or peak was observed (Fig. 2). Coulometric investigation revealed that four electrons are consumed by one molecule of **1a** at these pH values. Hence, the presence of one wave or one peak suggests that the reduction potentials of both nonprotonated thiadiazole rings are comparable in magnitude.

All these facts allow us to conclude that N=N bond in both heterocyclic rings of **1a** are reduced on mercury electrodes. We suggest three pathways for the electrode processes concerning thiadiazole **1a** (eq. 1): i) pH-dependence. The protonation of the reactant takes place prior to the first electron transfer and the process is partially controlled by the preceding protonation reaction (eq. 1a), (ii) pH-dependence. The protonated species are reduced and the first, one electron transfer process is followed by the slow protonation of an intermediates (eq. 1b) and iii) pH-independence (eq. 1c).

$$Th + H^+ \underset{k_b}{\overset{k_f = f(pH)}{\rightleftarrows}} ThH^+ + e \rightarrow ThH^{\cdot} + e \rightleftarrows ThH^- + H^+ \rightarrow ThH_2 \tag{1a}$$

$$Th + e \rightleftarrows Th^{\cdot -} + H^+ \underset{k_b}{\overset{k_f = f(pH)}{\rightleftarrows}} ThH^{\cdot} + e \rightarrow ThH^- + H^+ \rightarrow ThH_2 \tag{1b}$$

$$Th + e \rightleftarrows Th^{\cdot -} + e \longrightarrow Th^{2-} + 2H^+ \rightarrow ThH_2 \tag{1c}$$

During the electroreduction of water-organic **1a** solutions electrode reactions of peak c_1 in solution at pH < 3 and peak c_2 at all pH used occur *via* the "i" type mechanism (eq. 1a), whereas electrode reactions of peak c_1 at pH > 3 and polarographic wave are compatible with the "ii" type (eq. 1b). In acetonitrile reduction processes of **1a** proceed *via* "iii" type (eq. 1c).

The potential value of the first break on $E_{1/2}$ *vs.* pH and E_p *vs.* pH curves, so called "polarographic or voltammetric dissociation constants", $pK_1' = 3.6$ obtained in this work (Table 1) is quite close to average values of potentiometric dissociation constants of protonated species (pKa = 3.19 and pKa = 3.47 for both rings, respectively). However, a considerable discrepancy between the second polarographic and voltammetric value $pK'_2 = 6.8$ and these values and the corresponding potentiometric values of dissociation constants of thiadiazole neutral molecules (pKa = 9.66 and pKa = 10.16, respectively) were observed. According to the mechanism of **1a** reduction, suggested by us (eq. 1b), polarographic and voltammetric value $pK'_2 = 6.8$ is average value of dissociation constants of protonated radicals, which form during **1a** reduction.

Table 1. The values of the polarographic and voltammetric constants pKa' of thiadiazoles studied.

Compound	pKa'			
	polarographic		voltammetric	
	pK'_{a1}	pK'_{a2}	pK'_{a1}	pK'_{a2}
1a	3.6	6.8	3.4	6.7
1b	7.1	10.5	7.1	–
1c	6.0	–	5.9	–
1d	–	–	–	–

We observed that modification of the thiadiazole ring by spiro-annulation with tetramethylcyclobutanone containing electroactive carbonyl groups and replacement of the hydrogen atoms at carbon C-2 by methyl or *tert*-butyl substituents produce remarkable changes in mechanism of electrode processes.

One can expect that both N=N and C=O groups are electroactive under conditions described in this study. According to literature data [15,16], reduction of alkyl ketones requires strong negative potential. In the case of unsaturated alkyl ketones the C=C bonds are more easily reduced comparing with carbonyl group. Usually, a single 2-electron wave was observed, however in some cases, ketones exhibit two 1-electron waves [35,36]. It was found that the reduction process of carbonyl group strongly depends on steric factors [16,37–41].

During reduction of **1b** and **1c** in acetonitrile solutions three cathodic peaks c_1, c_2 and c_3 were observed, whereas only two peaks c_1 and c_2 were observed in the case of analogous **1d** reduction (Fig. 4). In acidic and neutral water-ethanol buffer solutions ($3 < pH < 7$) (Fig. 5) of **1b** two polarographic waves and two reduction voltammetric peaks c_1 and c_2 were observed. However, compounds **1c** and **1d** showed only one peak.

The potential and current of reduction peak of **1d** are pH-independent. Examination of Figures 6 and 7 reveals that potential for reduction of **1b** and **1c** are pH-dependent at pH < 7. From the observed dependence of the peak heights on pH, it is evident that the height of peaks c_1 and c_2 of **1b** is nearly constant, while that of **1c** decreases with increasing pH value. This result indicates that protonation of **1b** is fast, whereas that of **1c** is pH-controlled in acidic and neutral solutions. The ratio of the height of peak currents of peaks c_1 and c_2 of **1b** changes with pH, but the total wave and peak height remain constant. This result indicates that both processes are pH-dependent and dependent upon one another. Plot of $i_p/v^{1/2}$ *vs.* v, where v is the scan rate, indicates that the reduction current of peak c_2 has kinetic character (Fig. 8).

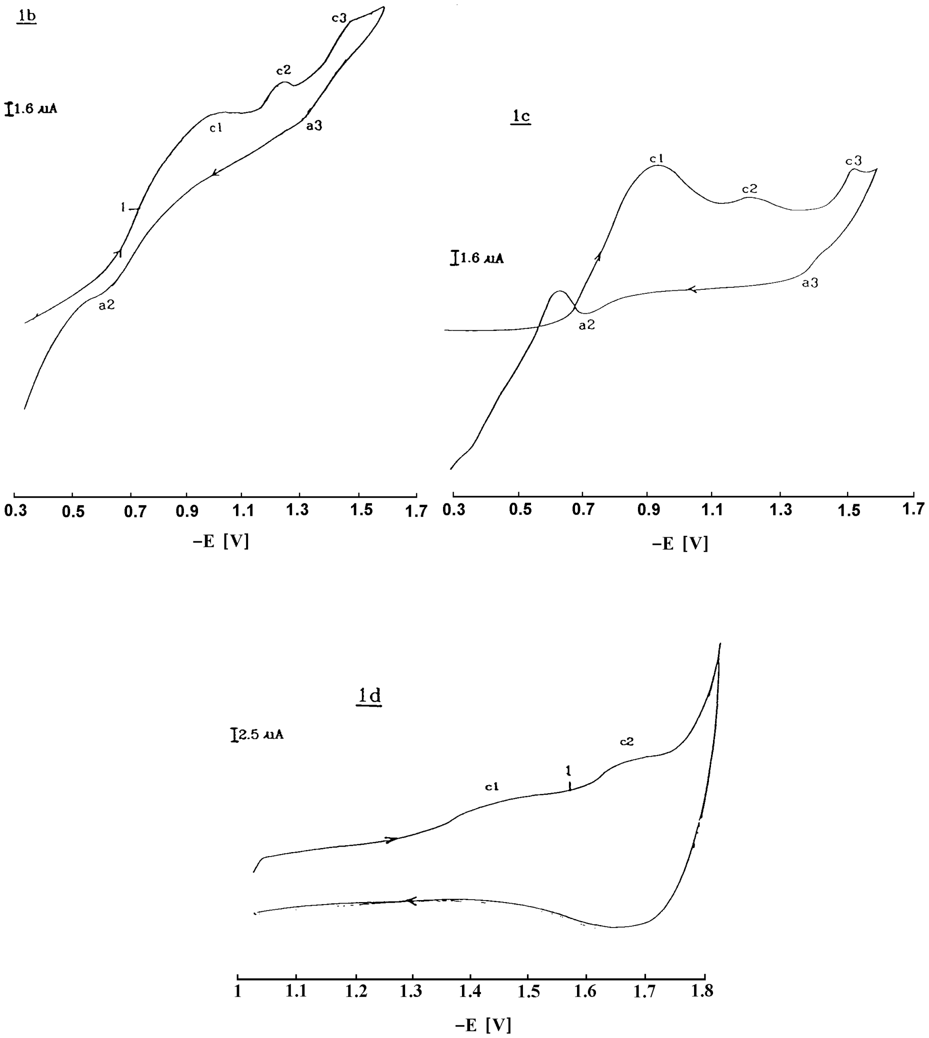


Figure 4. Cyclic voltammograms of 1×10^{-4} M **1b**, **1c** and **1d** in acetonitrile 0.1 M $LiClO_4$ solution. Sweep rate 200 mV/s.

The presence of surface phenomena in electrochemical processes of thiadiazoles is supported by the observation of plots of the ratio $i_p/v^{1/2}$ as a function of the scan rate "v" for peaks c_1 (Fig. 8). The nonlinearity of a plot presented in Figure 8 demonstrates the rate-controlled adsorption of depolarizers and is characteristic for an electrode process associated with a chemical reaction. Relationships between E_p values and log v for compounds investigated at the same concentration are linear. The slopes of the asymptotes are from *ca.* –20 mV/log unit at pH 2.2, *ca.* –45 mV/log unit at 3 < pH < 9 to –80 mV/log unit above pH 10. These results demonstrate that the process at pH = 2 is diffusion controlled, while that which occurs above pH > 3 is irreversible and has rather a surface character. Theoretically predicted values of the slope for a diffusion

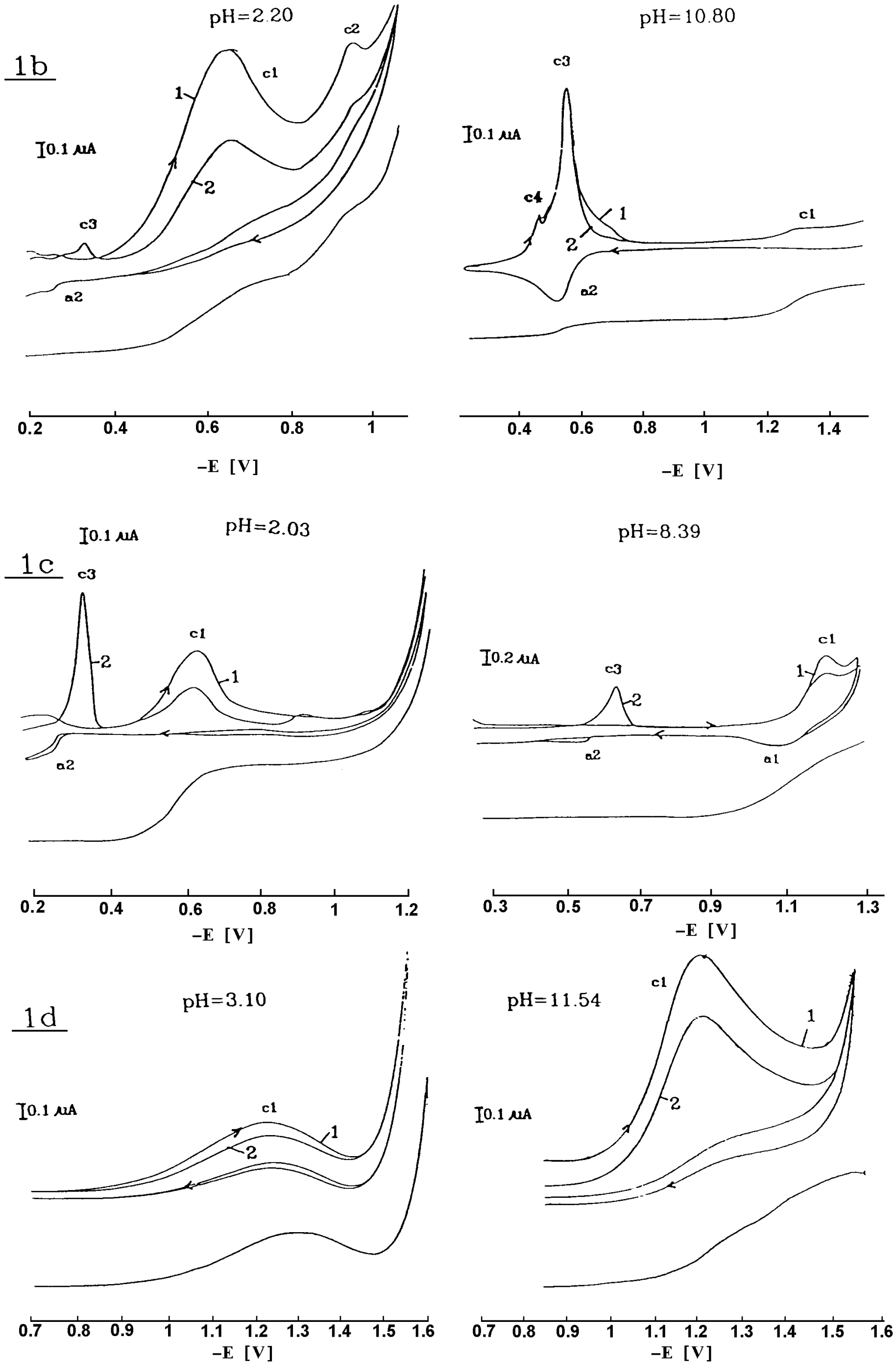


Figure 5. Variation of dc polarograms and cyclic voltammograms recorded during the reduction of 1×10^{-4} M: **1b**, **1c** and **1d** at different pH values. (1) first cycle and (2) second cycle. Sweep rate 200 mV/s.

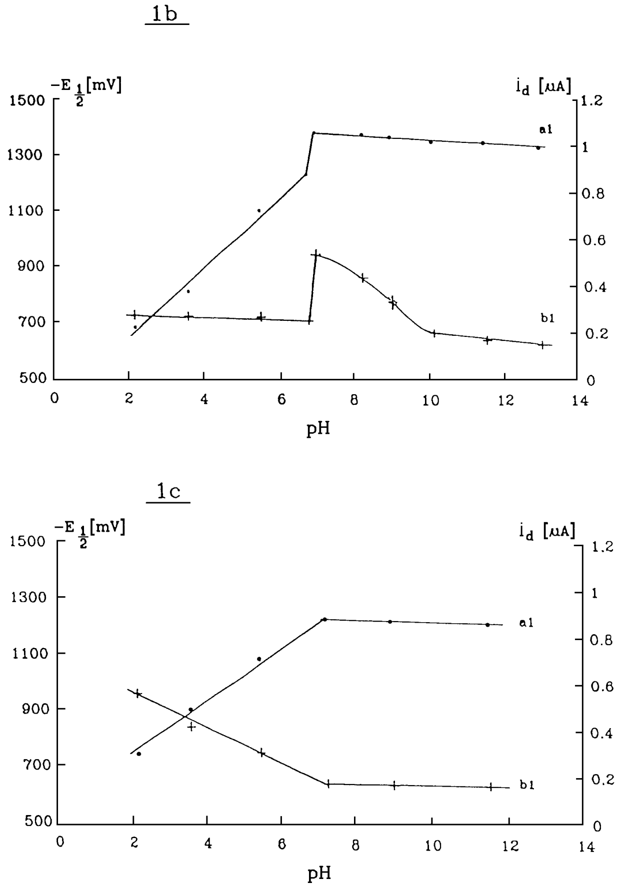


Figure 6. Dependence of half-wave potentials $E_{1/2}$ (a_1) and limiting currents i_l (b_1) on pH for 1×10^{-4} M **1b** and **1c** in Britton-Robinson's buffers.

controlled or surface reversible process are –18 mV/log unit and –36 mV/log unit, respectively [42,43]. The surface character of the electrode reactions is evidenced also by the fact that in subsequent polarization cycles peak c_1 decreased, while remaining peaks became more intense and finally all peaks approach the constant value. The third peak (c_2) observed during the reduction of **1b** and **1c** acetonitrile solutions corresponds probably to the adsorbed species reduction. Its adsorptive character supports this hypothesis.

All these facts indicate that the electrode reactions of **1b** and **1c** are analogous to that of **1a**. Hence, only the N=N bond is electrochemically reduced.

Therefore, at pH < 7, reduction process of the peak c_1 for **1b** and **1c** corresponds to irreversible reduction of protonated form of thiadiazoles to the corresponding thiadiazolidines according to the "i" type mechanism (eq. 1a). The reduction process of peak c_2 of **1b** corresponds to the reduction of molecules that result *via* dissociation of the protonated form of **1b** (eq. 1b).

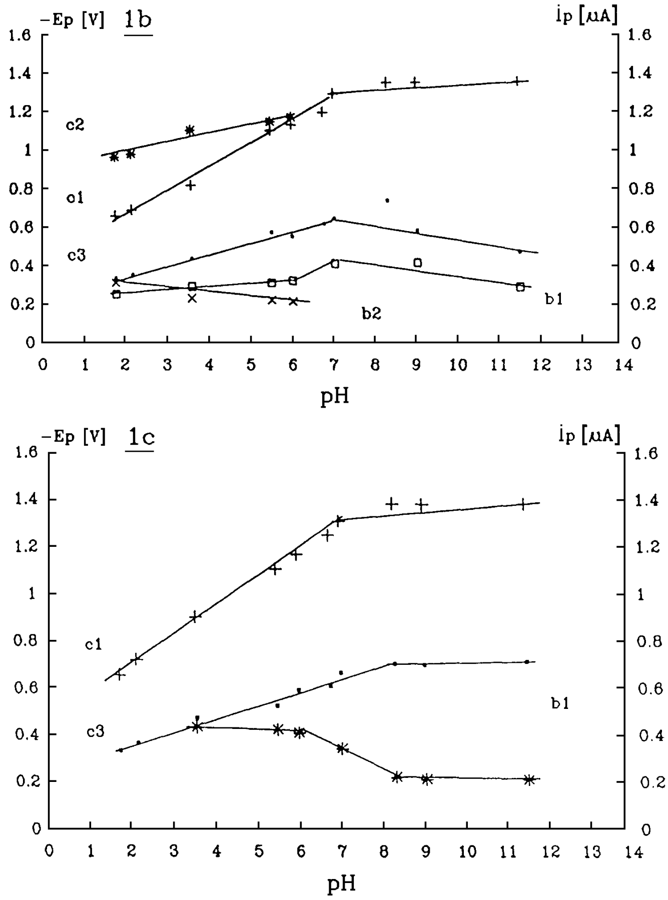


Figure 7. Dependence of peak potentials E_p (a_1) and peak currents i_p (b_1) on pH for 1×10^{-4} M **1b** and **1c** in Britton-Robinson's buffers.

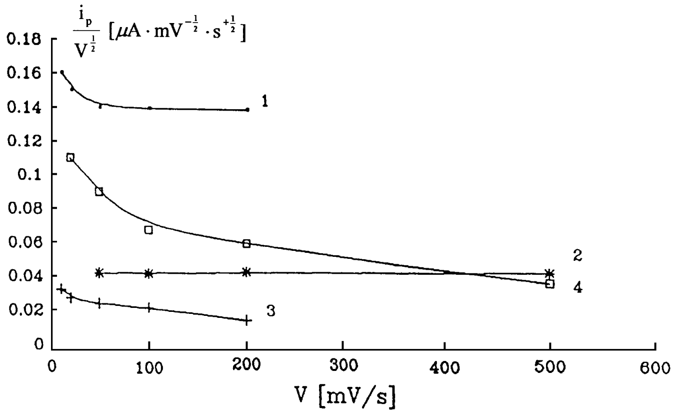


Figure 8. Plots of $i_p/v^{1/2}$ vs v for 1×10^{-4} M: 1) **1b** peak c_1, 2) **1b** peak c_2, 3) **1c** peak c_1 and 4) **1d** peak c_1. pH = 3.2.

At pH > 7 one wave is observed, which corresponds to the reduction of nonprotonated thiadiazoles **1b** and **1c** (eq. 1c). Compound **1b** exhibits only an 1-electron wave at pH > 9. It is likely that reduction of radical anion $A^{-\cdot}$ occurs at a potential that is too negative to be observed [31].

Compound **1d** exhibited quite different electrochemical behaviour in all solutions studied. Polarograms and voltammograms are untypical and difficult to interpret. The shape of cyclic voltammograms suggests that the electrode processes take place in the layer formed on the electrode surface, especially in acidic solutions (Fig. 4, **1d**). The reduction potential of **1d** was constant and pH-independent and no additional system of peaks were observed on voltammograms during second polarization cycle. The reduction potential value suggested that a nonprotonated form of N=N bond is reduced (eq. 1c).

In order to check above hypothesis 2×10^{-4} M acetonitrile solutions of **1a**, **1b**, **1c** and **1d** thiadiazoles were completely reduced by controlled potential coulometry at –1.8 V potential, and the final reduction products were isolated. The substances obtained thereby were investigated by IR and ^{1}H-NMR spectroscopic methods. Comparison of the IR spectra of electrolysis product with those of compounds before electrolysis demonstrated that the absorption band at 1580 cm^{-1} attributed to the N=N bond completely disappeared in the case of **1a**, **1b** and **1c** and was practically unchanged for compound **1d**. However, the ^{1}H-NMR spectra of the product after long-electrolysis of **1d** show spectra lines characteristic for hydrogen of hydrazo bond albeit the yield of the process is very small (*ca.* 10%) The C=O absorption band at 1780 cm^{-1} remained unchanged in **1b**, **1c** and **1d**. These results indicate that in the pH-range, used in this study, only N=N bonds underwent reduction process.

This suggestion is supported by results obtained during the electrochemical study of 2,2,4,4-tetramethyl-cyclobutane-1,3-dione using similar conditions as in the case of thiadiazoles. This compound displays two voltammetric reduction peaks at potential –1.8 and –2.3 V and both are far more negative than those observed during thiadiazoles reduction.

Hence, it is evident that the replacement of hydrogen atoms at C-2 by methyl groups produces smaller effect upon the electrode reduction mechanism of thiadiazoles than that observed in the case of replacement of hydrogen atom by *tert*-butyl groups. The presence of *tert*-butyl substituent in dihydro-thiadiazole molecule changes so much the steric and electronic properties of compound that makes the protonation and reduction of N=N bond much more difficult.

On cyclic voltammetric curves recorded during **1a**–**1c** and **1e** thiadiazole reductions on mercury electrode, an additional system of anodic-cathodic peaks (a_2 and c_3 in buffer solutions and reduction peaks c_3 and c_4 in aprotic media) and for **1a** acetonitrile-water solutions were observed in the second scan at more positive potential than that of the reduction peak c_1 and the half-wave potential of polarographic waves. The additional system of peaks is observed for **1a–c** in solutions at all pH values used in this study.

Figure 9 presents voltammograms of **1b** reduction during polarization of the electrodes in different potential ranges. It is evident that the reactions of peaks c_1 and c_2 of **1b** are mutually independent (Fig. 9; c.4 and 5) and that the oxidation reaction of the peak a_2 is conditioned by the reduction corresponding to peak c_1 or c_2 (Fig. 9; c.1, 2 and 3). In contrast, products of the oxidation reaction of peak a_2 are reduced in peak c_3 (Fig. 9; c.6). Similar dependence is observed on **1c** voltammograms.

We have previously discussed the presence of a similar additional system of peaks observed during the reduction of adamantane derivative **1e** [23] and we suggested that it results from chemical reaction between the mercury electrode and an intermediate product of the reduction of thiadiazoles. More extended discussion concerning the appearance of additional peak systems will be presented elsewhere.

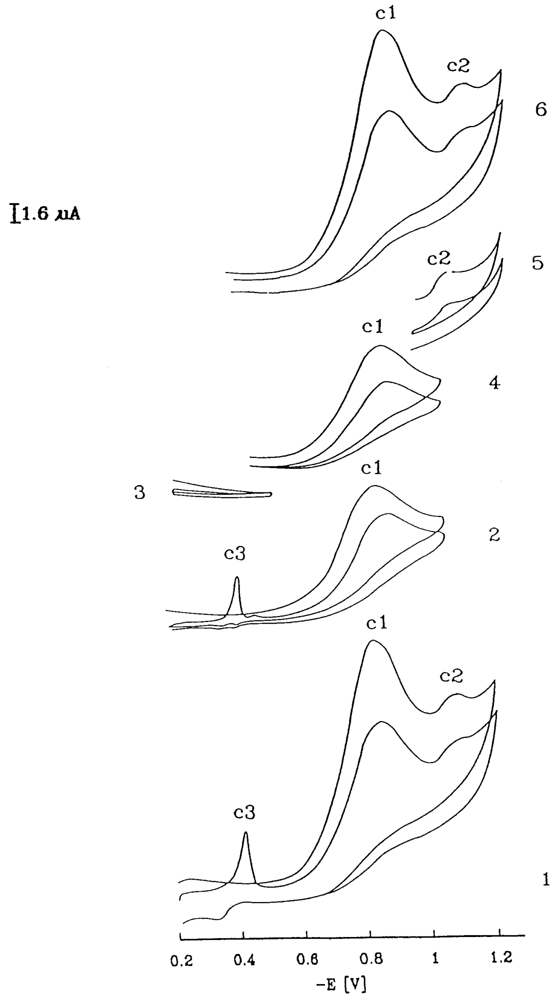


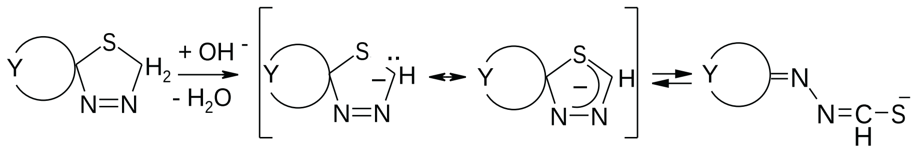
Figure 9. Cyclic voltammograms of 1×10^{-4} M: **1b** in Britton-Robinson's buffer at pH = 3.6 obtained in different sweep range. Scan rate 200 mV/s.

During the polarographic and cyclic voltammetric experiments performed with **1a** and **1b** in solution at pH > 9, a new reduction polarographic wave and a new voltammetric reduction peak c_5 at a potential of *ca.* –0.5 V were observed (Fig. 2). Similar peaks appeared during the electrochemical conversion of **1e** [23]. However, they were not observed during similar reduction of **1c** and **1d** derivatives. We suggested that these peaks may result from the reduction and oxidation of thiadiazole salts formed during electrochemical reduction directly in the solutions studied. Mloston and Huisgen [44,45] reported that the ring-opening of **1a**, **1b** and **1e** in basic solutions results in generation of thiol anion.

The ^{1}H-NMR spectrum of the product obtained in acetonitrile-water solutions of **1a** and **1b** at pH < 5 showed that ring-opening of these derivatives did not proceed under these conditions (two hydrogen atoms C_2 at σ 6.90 of **1a** and **1b** remained unchanged). However, at higher pH values, the corresponding bands completely disappeared. Hence, these dihydro-thiadiazoles **1** afforded thiadiazolidines (2,3,4,5-tetrahydro-1,3,4-thiadiazoles). Depending upon pH, compounds **1a** and **1b** convert into thiolates. This leads to the formation of electroactive thiadiazole salts on HMDE. Similar behaviour of diverse substances that contain thiol functional group (*i.e.*, SH) have been described in earlier publications [46–51].

Absence of the peak c_5 on the voltammograms of **1c** and **1d** is in agreement with results of potentiometric investigation of these dihydro-thiadiazoles, which indicate that (i) they do not possess acidic character under the conditions used and (ii) ring opening of these compounds did not take place [34]. This result confirms that in basic aqueous-ethanol and aqueous-acetonitrile solutions only the 2,5-dihydro-1,3,4-thiadiazoles with hydrogen atoms at C-2 undergo deprotonation according to route shown in Scheme 2.

Scheme 2



As can be seen in Figure 4, the ring-opening occurs easily in thiadiazole **1b** and at pH > 9 this compound exists as thiolate form, exclusively.

CONCLUSIONS

Obtained results indicate that modification of thiadiazoline ring by *their* combining with other systems and / or by the replacement of hydrogen atoms at carbon in position C-2 by methyl or *tert*-butyl substituents influences mechanisms of their electrode conversions.

Dihydro-thiadiazoles **1a**–**1c** studied in this work and also **1e** [23] were found to be reduced irreversibly to the corresponding thiadiazolidines. The reduction potential of

N=N bond decreased in the following order: **1e** >**1b** >**1a** > **1c** at pH < 4 and **1a** ≈ **1b** ≈ **1c** ≈ **1e**, at pH > 10. The sterically hindrance factor seems to be operating, as the less hindered azo groups are reduced more easily in acidic solutions. The bulky subsituted derivative **1d** seems to be reduced only in nonprotonated form. During the electrochemical processes in the molecule of derivative **1a** both N=N bonds are reduced.

In compounds studied N=N double bond is reduced in preference to the C=O group.

Electrochemical data obtained in the present study indicate that an additional system of peaks a_2 and c_3 observed on voltammetric curves during the electrolysis of compounds **1a**–**1c** and **1e** on HMDE results from the electrode processes involving organomercury compounds produced *via* chemical reaction of the mercury electrode with an intermediate product of N=N bond reduction.

The C-2 hydrogen atoms in 2,5-dihydro-1,3,4-thiadiazoles **1a**–**b** can be deprotonated in alkaline solutions. The opening of heterocyclic ring gives rise to a thiol anion, which reacts with cations, thereby affording electroactive salts. Potential values of peaks c_5 and a_4 suggested that they are responsible for reduction of these salts.

We hope that our study provides new evidence concerning the role of molecular structure and the adsorption of depolarizers in the course of electrochemical reduction or oxidation of sulfur-nitrogen-heterocycles in protic and aprotic media and enhances our knowledge about less known aspects of electrochemical conversions of these heterocycles.

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