VOLTAMMETRIC STUDY OF *N*-BENZOYLTHIOUREA AND ITS *N',N'*-DISUBSTITUTED DERIVATIVES AS POSSIBLE ELECTRODE MODIFIERS

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The voltammetric behavior of *N*-benzoylthiourea (BTU) and some of its *N',N'*-disubstituted derivatives is studied using glassy carbon and carbon paste electrodes in ethanolic solution. Irreversible reduction of the compounds takes place in a potential range between –0.5 and –1.1 V, where carbon surface groups are reduced as well. The products formed by reductive cleavage of the C–N bond of the amide group are oxidized in the subsequent positive scan at +0.5 V. Irreversible oxidation of the thiocarbonyl group of BTU (or its derivatives) takes place at about +1.0 V followed further by an oxidation of its *N',N'*-dialkyl and morpholine derivatives at more positive potentials. Oxidation current at +0.8 V is only observed in the case of the *N',N'*-diphenyl derivative. The oxidation current at +1.0 V depends linearly on the concentration of BTU (or its derivatives) and is suitable for their electroanalytical determination with carbon electrodes. The experimental results are compared with electrochemical behavior of related compounds. Furthermore, the influence of carbon surface states is discussed. It was concluded that *N',N'*-disubstituted derivatives of the BTU can be employed as modifying agents for carbon electrodes applicable in the potential range from +0.7 to –0.5 V.
Key words: Carbon paste electrode; Glassy carbon electrode; Chemical modification; Redox behavior; Thiourea derivatives; Cyclic voltammetry; Electrochemistry; Thioureas; Reductions.

The modification of electrode surface allows to design electrodes with desired chemical, electrochemical or other properties[1]. The modifying agent and the applied procedure depend on the intended application of modified electrode. Electrodes modified with suitable organic ligands allow the immobilization of metal ions at electrode surfaces for electroanalytical or other purposes. Ligands are selected according to their complexing ability, low solubility in the solvent and further properties which allow the preparation of electrodes with high selectivity and long-term stability[2–4]. The usage of ligands as modifying agents requires knowledge of their electrochemical redox behavior, which is the aim of this paper.
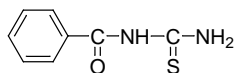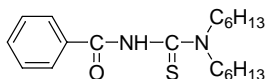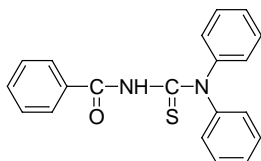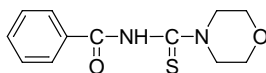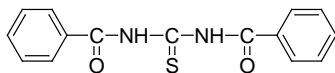
N',N'-Disubstituted derivatives of the N-benzoylthiourea (BTU) have attracted a considerable interest because of their ability to form complexes with thiophilic metal ions[5,6]. Practical applications can be found in the extraction of metals[7,8] and trace analysis of platinum metals[9]. The acidity of the BTU derivatives[6,10] as well as spectroscopic properties and stability of the metal complexes[6,11] were already thoroughly studied, whereas their electrochemical behavior remains nearly unknown. Cyclic voltammetry (CV) of the N',N'-diethyl derivative of the BTU at a glassy carbon electrode (GCE) in tetrahydrofurane was reported by Schuster[12]. Other authors stated that no redox peaks of BTU derivatives were observed at GCE in acetonitrile[13]. Recently, the voltammetric behavior of copper and nickel complexes of BTU derivatives at platinum electrodes was published[14,15], but no data concerning the redox behavior of ligands are given.

The absence of electrochemical studies of BTU and its derivatives is in contrast to studies of related compounds with thiocarbonyl or thioamide groups, such as thiobenzamides, thioamides or their N,N-disubstituted derivatives[16–20] on the one hand and to the intensively studied electrochemistry of the unsubstituted thiourea (TU) (*e.g.* refs[21–24,30]) on the other. Additionally, the application of N',N'-disubstituted BTU derivatives, *e.g.*, for the solvent extraction of thiophilic metals from industrial waste[6–8] requires suitable analytical methods for their determination. Usually, the BTU derivatives were determined by gravimetry, density measurement[7] or photometry[7,8].

Therefore, we started voltammetric studies in order to elucidate the electrochemical behavior of BTU and its N',N'-disubstituted derivatives. They can be characterized by CV either of the dissolved compound or of a composite electrode (*e.g.*, a carbon paste electrode (CPE) modified directly by an addition of the ligand). In this paper, electrochemical behavior of BTU and some of its typical N',N'-disubstituted derivatives is studied on GCE and CPE in ethanol–water mixture (4 : 1). N-Benzoyl-N',N'-dihexylthiourea (BDHTU), N-benzoyl-N',N'-diphenylthiourea (BDPTU) and N-(morpholine-4-thiocarbonyl)benzamide (MTBA) were chosen as BTU derivatives (*cf.* Scheme 1). Furthermore, the electrochemical behavior of N,N'-dibenzoylthiourea (DBTU) is presented for comparison. Simultaneously, the voltammetric determination of BTU derivatives should be checked.

The compounds under study are sparingly soluble in water, however, a protic solvent is still desirable for the study. Therefore, we used the ethanol–water mixture (4 : 1) as a solvent. The GC and the CP electrodes were used because we intended to modify carbon electrodes with the ligands un-

der study and also, carbon electrodes are more suitable for studies of sulfur-containing compounds than metal electrodes.

SCHEME 1

EXPERIMENTAL

A glassy carbon disk electrode (GCE) of 5 mm diameter (A_{GC} = 0.196 cm^2, Elektrokohle AG, Berlin) mounted in teflon and carbon paste electrode (CPE) (No. 6.0802.000, Metrohm, Filderstadt) with a diameter of 8 mm (A_{CP} = 0.503 cm^2) were used as working electrodes. The carbon paste was made from 3 g of graphite powder (RW-B, Ringsdorff, Bonn–Bad Godesberg) and 2 ml of paraffin oil ("Uvasol", Merck, Darmstadt) thoroughly mixed in an agate mortar. Both electrodes were smoothed by polishing before each experiment. The GCE was polished with a suspension of alumina (Chemiewerk Greiz–Dölau) in distilled water and then cleaned without polishing agent while CPE was smoothed using Teflon plate. The electrochemical cell was equipped with a working electrode, a Pt counter electrode (MC 20) and an Ag/AgCl (SE 20) or a saturated calomel electrode (SCE) (KE 20, both from Sensortechnik Meinsberg) as reference electrodes. The electrolyte solution was deaerated by bubbling with pure nitrogen before the experiment. Tetrabutylammonium perchlorate (TBAP puriss., Fluka, Neu–Ulm) was chosen as a supporting electrolyte and 80% aqueous ethanol as a solvent due to low solubility of compounds in water. The BTU derivatives under study are compiled in Scheme 1. BTU and its derivatives were synthesized according to Hartmann and Reuter[25] and recrystallized from pure ethanol. Their $1 \cdot 10^{-2}$ and $5 \cdot 10^{-2}$ mol l^{-1} stock solutions in absolute ethanol were freshly prepared.

The voltammograms were recorded with a potentiostat (Electrochemical interface SI 1286, Solartron–Schlumberger, Farnborough) equipped with PC and a plotter (HP 7440 "ColorPro", Hewlett–Packard) using the "DC CorrWare" (Scribner Assoc., Charlottesville, Virginia) software. Scan rates from 5 to 40 mV s^{-1} were used.

RESULTS

Cyclic voltammograms of the supporting electrolyte (0.2 M TBAP) in ethanol–water mixture at bare GCE are shown as the inset of Fig. 1. Characteristic features are the reduction current appearing in the range from –0.5 to about –1.0 V with the peak potential $E_p = -0.80$ V and steadily increasing oxidation current at positive potentials. In the first cycle the reduction current is higher and the current increase at $E > +0.5$ V is steeper. The CV of the supporting electrolyte measured at the CPE (not shown) is similar to that at the GCE, but the reduction current is higher with $E_p = -0.90$ V. Currents at the CPE are higher due to the larger electrode surface.

CV of N-Benzoylthiourea (BTU)

In Fig. 1 the CV of $2.5 \cdot 10^{-4}$ M BTU at the GCE is shown. Rather broad reduction peak with $E_p = -0.90$ V and one or two oxidation peaks appear. A well shaped oxidation peak at about +1.05 V can be found in each CV, whereas the broad oxidation peak appears only after a preceding sweep to potentials of the reduction.
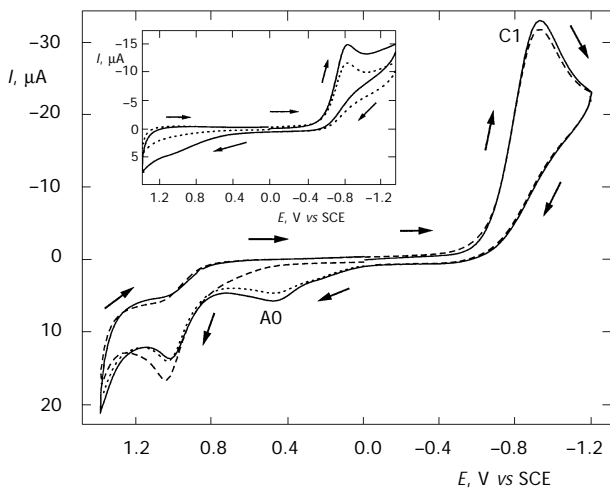
FIG. 1
CV of $2.5 \cdot 10^{-4}$ M BTU at GCE. 1st cycle from 0 to +1.4 V (– – –), subsequent scan from 0 to +1.4 V (· · · ·); 2nd cycle from 0 to –1.2 V (——). Supporting electrolyte 0.2 M TBAP. Solvent ethanol–water (4 : 1). Electrode surface polished prior to the 1st cycle. Scan rate 20 mV s^{-1}. *Inset*: CV of 0.2 M TBAP at the GCE in ethanol–water (4 : 1). 1st cycle from 0 to –1.4 V (——); 2nd cycle (· · · ·). Scan rate 20 mV s^{-1}. C1 Reduction current, A0 oxidation current

The reduction current (C1) appears in the same potential range as in solutions of the supporting electrolyte (Fig. 1) and the addition of BTU leads to its increase. At low concentrations of BTU ($c_{BTU} < 10^{-3}$ mol l^{-1}) the current increases with growing c_{BTU}. Furthermore, pretreatment at 0 V (while stirring the solution) leads (in the presence of BTU) also to an increase in C1 in the following scan, probably due to the adsorption of BTU on the GC surface. The current increase after pretreatment is steeper at $c_{BTU} < 10^{-3}$ mol l^{-1}.

The oxidation current A0 depends mainly on the negative reversal potential of the preceding cycle, whereas the concentration of BTU has little influence. But its maximum depends on the charge exchanged during the reduction (C1), indicating the oxidation of product(s) formed during the preceding reduction step. In the case of *N'*,*N'*-disubstituted BTU the oxidation peak A0 is more pronounced and appears at more positive potentials (Figs 4, 5). The appearance of an additional oxidation peak after a preceding application of negative potentials was recently observed at *N*-(diethylaminothiocarbonyl)benzamidines[26]. This group of compounds possesses the =N–CS–NR$_2$ functionality as the *N'*,*N'*-disubstituted BTU derivatives.

The peak current of A2 depends linearly on the concentration of BTU in the range from $6 \cdot 10^{-5}$ to $1.2 \cdot 10^{-3}$ mol l^{-1}. Voltammograms for different
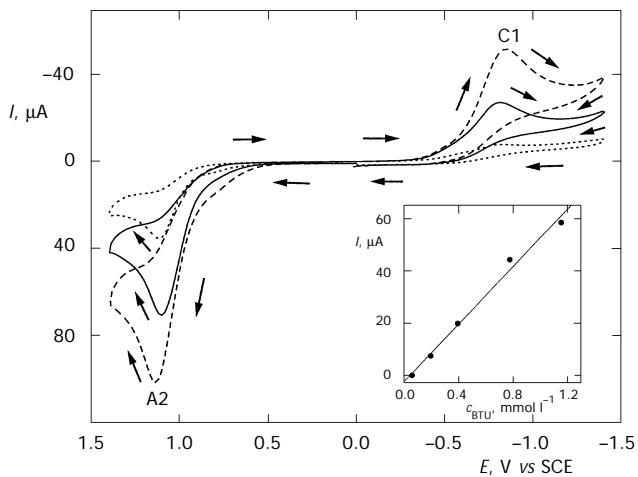

Fig. 2
CV of $4 \cdot 10^{-4}$, $8 \cdot 10^{-4}$, and $1.2 \cdot 10^{-3}$ M BTU at GCE. Cycles from 0 to +1.4 V. Electrode surface polished prior to each CV. For other conditions, see Fig. 1. *Inset*: Dependence of I_p (A2) on the concentration of BTU

c_{BTU} and the dependence of the peak current I_p on c_{BTU} are shown in Fig. 2. Here, CV is shown starting with a positive scan from 0 V. The slope of the I_p–c_{BTU} plot is $(55.0 \pm 3.2) \cdot 10^{-3}$ A mol^{-1} l with the intercept of $-(1.8 \pm 2.1) \cdot 10^{-6}$ ($r^2 = 0.995$). The dependence of I_p on c_{BTU} is linear even when a sweep to negative potentials precedes, but the slope of the I_p–c_{BTU} curve is by about 20% lower (*cf.* Fig. 1). The peak current I_p and the peak potential E_p of A2 are linear functions of the square root of the scan rate (in the investigated range from 5 to 40 mV s^{-1}).

Figure 2 shows the current C1 dependence on the concentration of BTU as well. The reproducibility of this part of curve is low due to a strong influence of the state of the electrode surface. The peak current of C1 increases approximately with the square root of the scan rate, whereas E_p varies only slightly ($|E_p| \approx v^{0.05}$).The same dependencies are found for the corresponding reduction peak in the supporting electrolyte.

The effect of polishing and preceding treatment is more pronounced at low c_{BTU}. The similar behavior was also observed in curves recorded immediately after polishing the GCE, but peaks are less pronounced and a current increase near C1 and at more negative potentials is observed. Since the current increase is also observed at polished GCE in the supporting electrolyte, it is assumed that the background current increases after polishing.
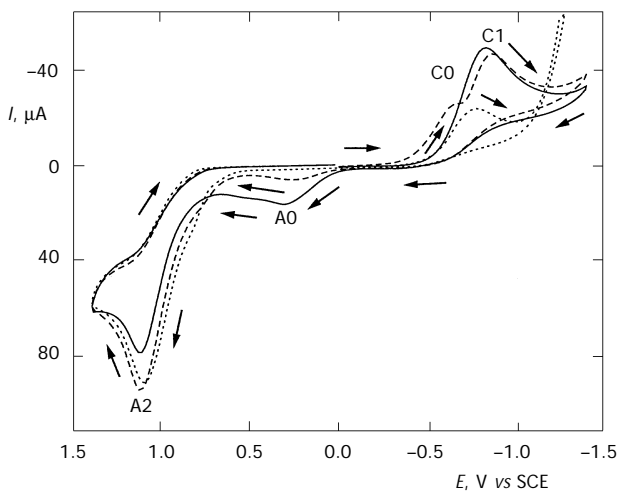

FIG. 3
CV of $2 \cdot 10^{-4}$ M BTU at GCE without and with addition of perchloric acid. Cycles from 0 to –1.4 V (——, – – –), to –1.2 V (· · · ·). Supporting electrolyte 0.2 M TBAP (——), with $1 \cdot 10^{-3}$ M HClO$_4$ (– – –), with $1 \cdot 10^{-2}$ M HClO$_4$ (· · · ·). Other conditions same as in Fig. 1

Preceding cycles lead to variations in the cathodic part of the subsequent voltammogram, in particular for low c_{BTU}. After a preceding cycle to potentials more positive than about +0.6 V, an additional reduction prepeak appears in the range from –0.5 to –0.6 V (not shown). The prepeak current increases with the value of positive reversal potential whereas the current C1 simultaneously decreases. In some cases a shift of the peak potential of C1 from –0.85 to –(0.55 … 0.60) V is observed after a preceding cycle to +1.4 V. The prepeak or shift is not observed in absence of BTU, indicating that it is caused by oxidation products of BTU formed at positive potentials and not by the oxidation of carbon surface groups.

Increased acidity of BTU solutions (by addition of perchloric acid) results in the appearance of reduction prepeak C0 and the simultaneous decrease (or disappearance) of the oxidation current A0 after a preceding sweep to negative potentials (Fig. 3). At pH 2 only a small reduction current between –0.5 and –0.9 V is observed followed by a sharp rise of the current, caused by the reduction of hydrogen ions. The main oxidation peak A2 is pH independent in the range from pH 2 to 7.

All voltammetric features of BTU found on GCE are also observed on CPE. The well-shaped oxidation peak (A2) appears at 1.10 V *vs* Ag/AgCl and the cathodic peak C1 shifts to positive potentials after a preceding sweep to potentials positive from peak A2. The peak current of A2 depends linearly on c_{BTU}. Experiments with sodium sulfate as supporting electrolyte reveal the same voltammetric behavior of the BTU.

CV of *N′,N′*-Disubstituted Derivatives of BTU and of N,N′-Dibenzoylthiourea (DBTU)

Electrochemical behavior of *N′,N′*-disubstituted BTU derivatives is similar to that of the unsubstituted compound, but additional oxidation currents are observed. In the case of the *N′,N′*-diphenyl derivative (BDPTU) an additional anodic peak (A1) with E_p = +0.82 V appears. It is better resolved while potential sweeped from 0 V to positive values than after scan to negative potentials. The other redox peaks are in accordance with those of BTU; peak currents of A1 and A2 depend on the concentration of BDPTU. At pH 2 peak A0 is not observed after preceding cathodic treatment. The other anodic peaks remain unchanged at low pH and the reduction peak shifts to more positive potentials.

In the CV of MTBA as well as of *N′,N′*-disubstituted BTU derivatives the peak A0 is more pronounced than in the case of unsubstituted BTU (Figs 4 and 5). Furthermore, an additional oxidation current (A3) appears at poten-

tials positive from A2. As examples voltammograms of $5 \cdot 10^{-4}$ M MTBA at GCE and of $5 \cdot 10^{-4}$ M BDHTU at CPE are shown in Figs 4 and 5.

No oxidation current of DBTU is observed at potentials up to +1.4 V. DBTU is reduced at about –1.0 V, where the peak potential depends on the
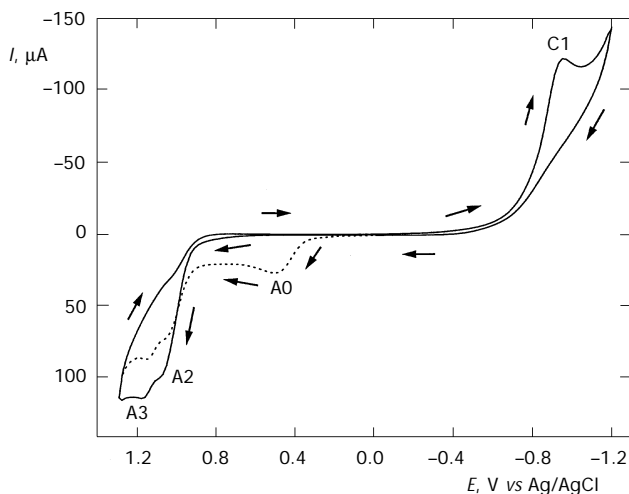

FIG. 4
CV of $5 \cdot 10^{-4}$ M DHBTU at CPE, start from 0 V. Supporting electrolyte 0.1 M TBAP. Other conditions same as in Fig. 1. 1st scan from 0 to +1.3 V (—), subsequent scan from 0 V (– – –)
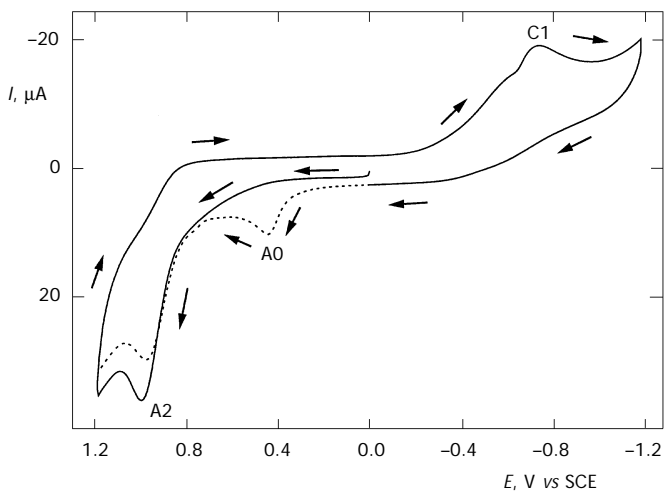

FIG. 5
CV of $5 \cdot 10^{-4}$ M MTBA at GCE; 1st scan from 0 to +1.2 V (—), subsequent scan from 0 to +1.2 V (– – –). Other conditions same as in Fig. 1

state of the electrode surface. Preceding oxidation causes a shift of E_p to more positive potentials (Fig. 6). After a preceding cycle to negative potentials, pronounced oxidation peak A0 is observed at +0.65 V (Fig. 6). Its peak current depends again on the negative reversing potential or cathodic treatment. The voltammetry of the unsubstituted TU is shown in the inset of Fig. 6.

DISCUSSION

BTU and their derivatives are multifunctional organic compounds (Scheme 1) which contain an amide, thioamide as well as NH_2 group (in the case of the unsubstituted BTU) or NR_2 group (in the case of the *N'*,*N'*-disubstituted derivatives). Therefore, both reduction and oxidation can take place at different functional groups and reactions of all the products have to be taken into account together with the influence of carbon surface groups.

The reduction current C1 of BTU is observed in the potential range where the reduction of glassy carbon surface groups occurs (Fig. 1 and inset) which indicates that carbon surface groups are involved in the reduction of BTU and its derivatives. Specific interactions of reactants with surface groups on the GC were observed in the reduction of carbonyl compounds on GCE (refs[27–29]). Furthermore, strong adsorption of the unsubstituted TU
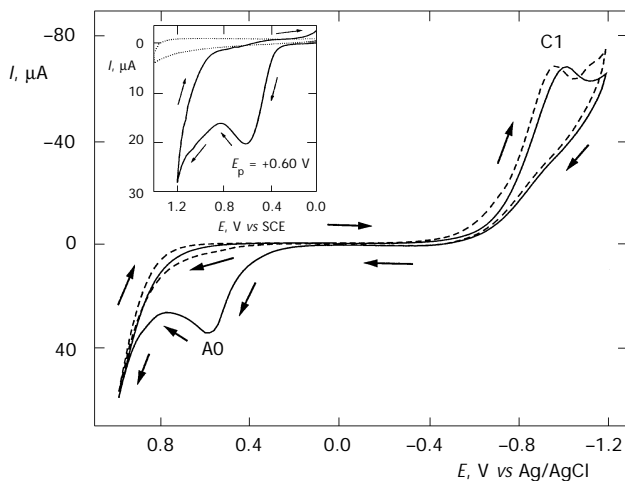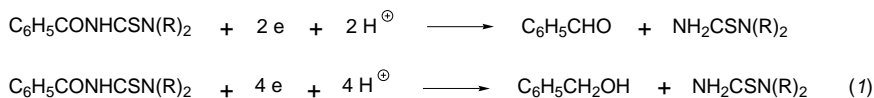

Fig. 6

CV of $1.0 \cdot 10^{-3}$ M DBTU at GCE. 1st scan from 0 to +1.0 V (– – –), from 0 to –1.2 V (——). Other conditions same as in Fig. 1. *Inset*: CV of $1.4 \cdot 10^{-4}$ M TU (——), and the supporting electrolyte at GCE (– – –)

on carbon electrode was concluded from voltammetric studies[22,30]. But the reduction of amides, thioamides or derivatives of TU at GCE was not yet described. The observed "amplification" of the cathodic current in the presence of BTU points to the participation of carbon surface groups in the reduction. The significance of surface groups in the reduction of compounds under study will be discussed later.

Normally, the cathodic reduction of amides leads to unstable geminal hydroxyamines which react further to the corresponding amines and primary alcohols or aldehydes depending on the structure and the reaction conditions[31,32]. Benzamide is reduced (at Hg electrodes) with cleavage of the C–N bond, where a radical anion is formed which is subsequently protonated (in case of EtOH the solvent itself is the proton donor)[33]. The cathodic reduction of amides leads in the presence of tetraalkylammonium (TAA) ions to amines and alcohols[34], where electron transfer proceeds *via* TAA radicals. The reaction is very selective in the case of aryl substituted amides[31] and is used to remove protecting groups such as the benzoyl moiety by reductive cleavage[35,36].

The oxidation current (A0) is observed at positive potentials with a current maximum at about +0.5 V after a cathodic treatment (Figs 1, 4 and 5). The anodic oxidation of the unsubstituted TU at GCE occurs in aqueous solution in the potential range from +0.3 to +0.9 V with E_p at +0.60 V (refs[22,30]), which is confirmed by measurements in ethanol–water[37] (*cf.* inset of Fig. 6). Therefore, it is assumed that BTU and its derivatives are cathodically reduced under cleavage of the C–N bond of the amide group and the formation of TU or the corresponding *N,N*-disubstituted thiourea takes place according to Eq. (*1*).

$$C_6H_5CONHCSN(R)_2 \ + \ 2\,e \ + \ 2\,H^\oplus \ \longrightarrow \ C_6H_5CHO \ + \ NH_2CSN(R)_2$$

$$C_6H_5CONHCSN(R)_2 \ + \ 4\,e \ + \ 4\,H^\oplus \ \longrightarrow \ C_6H_5CH_2OH \ + \ NH_2CSN(R)_2 \qquad (1)$$

$$R = H, \text{ alkyl or aryl group}$$

The oxidation current A0 during the next sweep towards positive potentials is then caused by the oxidation of TU or *N,N*-disubstituted thiourea formed in reaction (*1*). Anodic oxidation of TU in acidic solution yields salts of the formamidine disulfide[21,38,39]. The oxidation of the *N*-alkyl or *N*-acyl derivatives of TU produces corresponding derivatives[23,38]. Although thioamides are cathodically reduced in a more complicated reaction[16], the reductive cleavage of C–N bond (and formation of *N,N*-disubstituted TU) is

possible for the BTU derivatives. But in the case of BTU an additional current is observed in the range from 0 to about +0.7 V besides the peak A0 (*cf.* Fig. 1) in contrast to *N′,N*-disubstituted derivatives (Figs 4 and 5). The unsubstituted TU shows an additional oxidation current (in the range from 0 to about +0.5 V) after a preceding sweep to negative potentials[37]. Presumably it is caused by the adsorption and consecutive reactions of products of the preceding reduction. Possible reactions are sulfur–oxygen exchange or the decomposition of dithioformamidine derivatives. It is known that dithioformamidines decompose in solutions of low acidity to cyanamide, sulfur and TU (refs[22,39]) and that sulfide elimination occurs during the reduction of thiones in aqueous solution[16,40]. At carbon electrodes the participation of TAA cations (or TAA radicals) in the cathodic reduction is discussed[41,42], but experimental results do not allow to formulate the conclusion concerning the role of TAA ions in the reduction (*1*).

In contrast to the unsubstituted TU, which is oxidized at about +0.6 V (Fig. 6), DBTU is not oxidized at GCE at potentials up to +1.4 V. Since on the other hand, BTU and its derivatives are oxidized at about +(1.1 ± 0.1) V (Figs 1, 2, 4 and 5), it is concluded that the oxidation potentials shifts about 0.5 V to more anodic potentials when one NH_2 group of the TU is substituted by $-NHCOC_6H_5$. For this reason, the oxidation of DBTU is not observed. A similar shift of the redox potential of ferrocene derivatives was found after introduction acyl groups[43].

The oxidation of BTU with bromine to *N,N′*-dibenzoyl-1,1′-dithiobisformamidine dihydrobromide[44] confirmed that oxidation of TU derivatives yields derivatives of the formamidine disulfide. Therefore, it is assumed that the current A2 is caused by the oxidation of thiol group of BTU to *N,N′*-dibenzoyl-1,1′-dithiobisformamidine or to the corresponding dication (according to Eq. (*2*)). The formation of the dithiobisformamidine dication is more probable since the peak current A2 does not depend on pH. The anodic oxidation of thiol group at these potentials is known also for other compounds with thiol groups, for example the 2-sulfanylbenzothiazole[45]

$$2\ C_6H_5CONHCSNR_2 \longrightarrow \begin{array}{c} C_6H_5CO\overset{\oplus}{N}H{=}CNR_2 \\ | \\ S \\ | \\ S \\ | \\ C_6H_5CO\overset{\oplus}{N}H{=}CNR_2 \end{array} \quad +\ 2\ e \qquad (2)$$
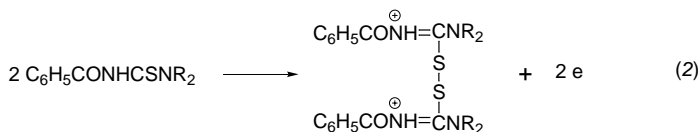
As outlined, the peak potential E_p and peak current I_p of A2 depend in a good approximation on the square root of the scan rate, indicating that the

diffusion of BTU is the rate determining step. The decrease in the peak current of A2 after a preceding sweep to negative potentials (Fig. 1) is probably attributed to the adsorption of BTU or its reduction product at the electrode. Strong adsorption of the reduction product is probable, since the peak current of A0 depends on the duration of the cathodic treatment, whereas the influence of the concentration of BTU (or BTU derivative) is low. The adsorption of TU at carbon electrodes was already mentioned in the literature[22,30].

Information concerning the charge transfer step of irreversible electrode reactions can be obtained from the difference $E_p - E_{p/2}$ or from the shift of E_p with the sweep rate v (refs[46,47]). Determination of αn for the irreversible oxidation of BTU at A2 yields $\alpha n = (0.38 \pm 0.02)$ and n = (0.76 ± 0.04) for α = 0.5, whereas α = 0.35 and n = (0.70 ± 0.10) with α = 0.5 are obtained from the slope of E_p *vs* log v (at different concentrations from 5 to 40 mV s^{-1}). The values found for αn and *n*, respectively, allow to conclude that n = 1 is the most probable value even for relatively narrow range of *v*. The transfer of one electron per reacting molecule to the electrode is also in an accordance with Eq. (*2*).

The shift of peak C1 to more positive potentials or corresponding prepeak is attributed to oxidation products. The prepeak or shift is not observed in absence of BTU. Dithiocarbenium salts, formed by the oxidation of tetraalkyl substituted TU, are reduced at about –0.5 V *vs* Ag/AgCl (ref.[48]). Therefore, the additional reduction current could be caused by the reduction of dithioformamidine derivatives formed according to Eq. (*2*).

The oxidation current A3 observed for the N',N'-dialkyl derivatives and the MTBA (Fig. 5) indicates that the product of the anodic oxidation A2 is further oxidized at higher anodic potentials ($E_p \approx$ +1.2 V). It is known, that the dithiobisformamidine derivatives can be oxidized anodically[45] or with bromine[44]. During this reaction the cleavage of the S–S bond of the disulfide takes place under formation of various oxidation products[45].

The oxidation peak A1 at +0.8 V is only observed in voltammograms of BDPTU at CPE and GCE. Tertiary amines with at least one phenyl group on the amine nitrogen are oxidized at about +0.8 to +0.9 V *vs* SCE (ref.[49]) and the oxidation peak is observed only in the presence of BDPTU. Thus, it can be concluded that the oxidation current is due to the oxidation of the NR$_2$ group in BDPTU in accordance with known stability of cation radicals of aromatic amines[50].

The influence of surface groups to electron transfer at carbon electrodes is well known[51]. In particular, electrode reactions of metal ions and metal complexes at GC are studied intensively[52], whereas the role of surface

groups on the electrochemical reactions of carbonyl compounds at GC has not received much attention. Chandrasekaran *et al.*[29] studied the reduction of benzaldehyde at GC and observed in neutral aqueous media a cathodic prewave caused by the protonated benzaldehyde or by the interaction of the radical anions of benzaldehyde with acidic surface groups (depending on the solvent and pH). The authors discussed the protonation of benzaldehyde by acidic surface groups (surface protonation model) and pointed out that the radicals formed are adsorbed on the GC surface. A shift of the reduction potential was also observed in the reduction of 2,4,6-trimethylbenzaldehyde at GCE after the addition of acetic acid[53].

The additional reduction peak C0, observed after addition of perchloric acid (Fig. 3), can be caused by the protonation of surface groups and/or by the protonation of BTU or an intermediate. The protonation of the C=S group of the BTU is possible in acidic solution and the thiol form of thiocarbonyl compounds is reduced at potentials considerably more positive than the corresponding thione[40]. Therefore, peak C0 can be attributed to the reduction of protonated BTU, where the reduction products formed are different from those in neutral solution. On the other hand, protonated surface groups can participate on C0 reduction since their concentration is enhanced in acidic solution. The dependence of the course of cathodic reaction on the surface state of the GC is confirmed by the alterations of C0 and C1 after previous application of positive potentials. Further experiments, however, are necessary to elucidate the exact kinetics of the reduction and the participation of carbon surface groups.

CONCLUSIONS

BTU and its *N′,N′*-disubstituted derivatives were characterized by voltammetry on carbon electrodes for the first time. From the experimental data it is concluded that compounds under study are reduced in the range from –0.5 to –1.2 V (E_p at about –0.80 V for GCE and between –0.8 and –1.1 V for CPE). During the reduction cleavage of C–N bond of the amide group takes place. TU or its *N,N*-disubstituted derivative is then oxidized in subsequent positive sweep with current maximum between +0.3 and +0.6 V). The main oxidation peak, appearing at about +1.10 V, corresponds to the oxidation of the thiocarbonyl group. In the case of *N′,N′*-dialkyl derivative and MBTA the oxidation product is further oxidized at more positive potentials.

The voltammetric curve depends on the state of the electrode surface as well as on previously applied potentials. The increase in the reduction cur-

rent after pretreatment is attributed to the adsorption of BTU or its derivatives. First results on the influence of solution pH are reported. The reactions of BTU derivatives could not be elucidated in detail, but the study was mainly directed to the applicability of presented compounds as electrode modifiers. The electrochemical behavior of ligands is also of interest for studies of their metal complexes.

Only the ligands which electrochemical behavior is known can be used for the modification of electrode surfaces. According to our experimental results, BTU and its derivatives can be employed as modifying agents. The applicable potential window was found to be in the range from +0.7 to –0.5 V. Outside this range, redox reaction of the modifier itself will interfere. Electrodes modified by BTU derivatives can be used for the immobilization of noble metals. Thus, Ag^+ was immobilized on CPE modified with N-benzoyl-N',N'-dibutylthiourea[54]. The study confirms also the suitability of BTU derivatives as modifiers for immobilization of thiophilic metal ions, especially Pd^{2+} and Cu^{2+}. Modification process can be extended to GC or other carbon based electrode materials.

The voltammetric characterization of modifying agents can be done either by a solution voltammetry or with a modifier added to a composite electrode. Especially for insoluble compounds, the second way yields good results as demonstrated for tetrathiafulvalene derivative[55]. On the other hand, the solvent used for the characterization of soluble compounds may be different from that in which the modified electrode will be used.

The linear dependence of the peak current A2 on the concentration of BTU (BTU derivative) enables their voltammetric determination in a wide concentration range, which is of importance for solvent extraction.

SYMBOLS

A	electrode area
A0, A1, A2, A3	anodic peaks or anodic currents
BDHTU	N-benzoyl-N',N'-dihexylthiourea (*cf.* Scheme 1)
BDPTU	N-benzoyl-N',N'-diphenylthiourea (*cf.* Scheme 1)
BTU	N-benzoylthiourea (*cf.* Scheme 1)
c_{BTU}	concentration of the N-benzoylthiourea
CP, CPE	carbon paste, carbon paste electrode
CV	cyclic voltammetry
C0, C1	cathodic peaks or cathodic currents
DBTU	N,N'-dibenzoylthiourea (*cf.* Scheme 1)
E	electrode potential
E_a	anodic reversal potential
E_p	peak potential

I	current
I_p	peak current
GC, GCE	glassy carbon, glassy carbon electrode
MTBA	*N*-(morpholine-4-thiocarbonyl)benzamide (*cf.* Scheme 1)
n	number of electrons
TAA	tetraalkylammonium
TBAP	tetrabutylammonium perchlorate
TU	(unsubstituted) thiourea
v	scan rate
α	transfer coefficient

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