ORIGINAL PAPER

Adsorption and electro-oxidation of *N*-alkyl and *N,N'*-dialkyl thioureas on gold electrodes in acid solutions. A combined FTIRRAS and voltammetry study

A. E. Bolzán · A. J. Arvia

Abstract The adsorption and electro-oxidation of *N*-alkyl and *N,N'*-dialkyl thioureas on polycrystalline gold in aqueous acid solutions is studied by Fourier-transformed infrared reflection absorption spectroscopy (FTIRRAS) and voltammetry. The potential ranges for different electrochemical processes, including electrodissolution of gold and electro-oxidation of thioureas, are determined by cyclic voltammetry. The gradual depletion of thioureas and the progressive formation of products from adsorbed and soluble species in the thin solution layer in contact with the electrode are followed through changes in band intensity of infrared (IR) spectra. Adsorbates of thioureas are formed at 0.05 V and remain on the surface up to $E=1.2$ V, a potential at which their electro-oxidation takes place. Irrespective of the type of thiourea, the first electro-oxidation process from soluble thioureas starts at ca. 0.45 V with the formation of their respective disulphide. This process is preceded by the electrodissolution of gold via the formation of gold–thiourea soluble complex species. From ca. 1.2 V upwards the second electro-oxidation process results in the formation of carbon dioxide, sulphate ions and C≡N-containing species. The latter are produced only from *N*-alkyl thioureas, in which the presence of free amine groups makes the formation of a C≡N bond possible, as a previous stage to the production of carbon dioxide and sulphate ions as final products. From the correlation between voltammetric and spectroscopic data a general reaction pathway for the adsorption of thioureas and their electro-oxidation on gold is advanced.

This work is dedicated to Prof. Teresa Iwasita on the occasion of her 65th birthday.

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Introduction

Substituted thiourea (*s*-TU) derivatives have attracted attention because of their potential use as reagents for the separation of metal ions [1]. From the electrochemical point of view, the formation of *s*-TU–metal complexes are also of potential interest in metal electrodeposition [2] and corrosion inhibition [3–5].

Metal complexes with *s*-TU ligands have been reported for a number of metals such as copper [6, 7], platinum [8], palladium [8], zinc and cadmium [8, 9]. The *s*-TU derivatives have, as possible donor sites, the sulphur atom of the C-S group and the nitrogen atom of the NH, NHR or NRR' groups (where R=R'=alkyl or dialkyl groups). Furthermore, molecules with the coplanar N₂CS skeletal atoms such as *N*-alkyl thioureas, exhibit trans and cis conformational forms, whereas for *N,N'*-dialkyl thioureas *cis–cis*, *trans–trans* and *cis–trans* isomers become possible. These structures make their molecular adsorption at different positions on solid metal surfaces possible. This makes it attractive to investigate physicochemical aspects of these compounds to be used as additives for improving metal electroplating and metallic corrosion inhibition [10–12].

As for thiourea (TU), *N*- and *N,N'*-substituted thioureas (*s*-TU), particularly those bearing at least one hydrogen atom, exist in tautomeric thiolate forms, i.e.

$$R_1HNC(=S)NHR_2 \rightarrow R_1HNC(SH)NR_2 \qquad (1)$$

yielding metal thiolate-type ligands. Consequently, they are readily adsorbed on metals via a metal–sulphur bond, the

strength of this bond depending on both the solution composition and the electric field at the metal–solution interface [13, 14].

Soluble TU- and s-TU-containing metal complexes can be formed electrochemically [15, 16] via surface complex intermediates, acting as precursors of the course of metal electrodissolution. Products of this type have been found for a number of metals in acidic solutions [17–26], even in the absence of amine hydrogen in the s-TU, as tetramethylthiourea (TMTU).

On the other hand, both TU and s-TUs can be oxidised to the respective formamidinium disulphide (FDS) by either chemical or electrochemical methods. For instance, oxidation reactions by hydrogen peroxide have been used to convert N-alkylthioureas to N,N-dialkylated dithioformamide [27, 28]. The electrochemical formation of dithioformamidinium species from the electro-oxidation of TU and TMTU on platinum [29–31] and gold electrodes [32] has been reported.

Recently, a comparative study of the electro-oxidation of TU and methyl-TUs on platinum in acid [30] showed that both reaction pathways involve a potential regions below 1.0 V, where the respective FDS is formed, and another one, above 1.0 V, yielding carbon dioxide, sulphate ions and cyanamide species as products from the complete electro-oxidation of those molecules. However, an important difference between platinum and gold electrodes is that no evidence of soluble TU- and s-TU–platinum complex anodic formation has been observed.

This work is devoted to a comparative study of N-alkyl and N,N'-dialkyl thioureas electro-oxidation on gold in acid, particularly concerning with the kinetics and mechanism of adsorption, and the electro-oxidation TU and s-TU on polycrystalline gold. Through the in-situ determination of soluble electro-oxidation products at different applied potentials, and the comparison to data previously reported for platinum electrodes, a likely global reaction pathway for TU and s-TU electro-oxidation on gold, involving the participation of both homogeneous reactions in solution and surface electrochemical reactions including adsorption processes, is proposed.

Experimental

Electrochemical measurements

Voltammetric runs were made utilising a conventional three-electrode electrochemical glass cell that included a polycrystalline gold wire working electrode (J. Matthey, spec pure, geometric area, 0.25 cm^2) a platinum counter electrode, and a mercurous sulphate reference electrode (MSE). Previous to each measurement, the working electrode was polished with

an alumina (0.3 μm grit)–water suspension, and thoroughly washed with Milli-Q* water.

Voltammetric runs were performed using either plain aqueous 0.1 M perchloric acid or aqueous 1 mM s-TU + 0.1 M perchloric acid. Solutions were prepared from Milli-Q* water, perchloric acid (70% Merck, p.a.), N-methyl thiourea (MTU), N,N'-dimethyl thiourea (DMTU), N-ethyl thiourea (ETU) and N,N'-diethyl thiourea (DETU) (all Fluka, puriss. p.a.). For each experiment freshly prepared solutions continuously kept under nitrogen (99.99%) saturation were used.

Voltammetry was run with a Radiometer Voltalab 10 potentiostat. All runs are referred to the standard hydrogen electrode (SHE) potential scale.

FTIRRAS measurements

The electrochemical cell for in situ Fourier-transformed infrared reflection absorption spectroscopy (FTIRRAS) measurements consisted of a conventional three-electrode design [33], with a fluorite 60° prism at the bottom of the cell. A polycrystalline gold disc (1.2-cm diam.) was used as the working electrode. Before each run, this electrode was polished to mirror grade with 0.3 μm grid alumina and rinsed with Milli-Q* water. A platinum sheet and a reversible hydrogen electrode in the working solution were used as counter and reference electrode, respectively.

For FTIRRAS the concentration of TUs was set to 0.1 M to obtain significant changes in the spectra of the thin solution layer in contact with the working electrode. In a first set of spectra aqueous 0.1 M X + 0.1 M perchloric acid (X = MTU, DMTU, ETU, DETU) were used. Solutions were prepared from perchloric acid (70% Alfa Aesar, p.a.) and Milli-Q* water. Spectra were also recorded utilising 0.1 M sulphuric acid (Mallinckrodt AR, 99.9%) in deuterium oxide to investigate the FTIRRAS region where water bands overlap those of s-TU and their respective disulphides.

Spectra from freshly prepared nitrogen-saturated (P_{N2}= 1 atm) solutions were run to minimise the influence of byproducts resulting from a possible spontaneous decomposition of s-TU. Measurements were performed using a Nicolet Nexus 670 FTIR spectrometer coupled to a Wenking 72L potentiostat. Each set of spectra was obtained by increasing the applied potential 0.05 V stepwise from 0.05 to 1.6 V. At each potential 256 interferometer scans with 8 cm^{-1} resolution were collected. Normalised reflectance spectra were calculated as R/R_0 ratio, where R is the value of the reflectance at the sampling potential E_s and R_0 is the reflectance measured at the reference potential, E_{ref}=0.05 V.

Spectra with either p- or s-polarised light were recorded to collect data either from both soluble and adsorbed species or exclusively from soluble species in the thin solution layer. However, as the same bands are involved in

both *p*- and *s*-polarised light spectra, only the former ones are shown. Positive and negative absorption bands represent the loss and gain of species at E_s as compared to E_{ref}, respectively. All runs were performed at 298 K and potentials in the text are referred to the SHE scale.

Results

Voltammetric data

Voltammograms of N-alkyl and N,N'-dialkyl thiourea in aqueous 0.1 M perchloric acid

In general, for all the *s*-TU, the positive-going potential scan from stabilised voltammograms run at 0.05 V s^{-1} between 0.05 and 1.6 V (Fig. 1) show a negative current up to ca. 0.3 V followed by an anodic current that reaches a small peak I_a at ca. 0.70±0.05 V, a large current plateau that extends from ca. 0.8 to 1.1 V, and eventually a large current peak II_a at ca. 1.4 V. The subsequent reverse scan also shows a cathodic current peak II_c at ca. 1.05 V, mainly due to the electroreduction of the gold oxide adlayer [34] followed by decrease in current to almost zero, and from ca. 0.65 V downwards, the cathodic peak Ic in the range 0.20–0.35 V.

When the potential scan goes from 0.05 to 0.95 V (Fig. 2) the pair of peaks I_a and I_c become better defined. For ETU, a

second cathodic current peak I'_c is also recorded. For other *s*-TUs, a residual contribution of this peak is hardly visible as a small hump on the left side of peak I_c. This asymmetric behaviour of peak Ic is likely due to the overlapping of at least two closely located cathodic current peaks.

As it has been reported for TU on platinum [29], copper [35] and gold [36–38] and for TMTU on platinum [30] and gold [32], conjugated current peaks I_a/I_c are related to the *s*-TU $\rightleftharpoons$ *s*-FDS redox process. This assignment is also consistent with the fact that [RSSR]$^{2+}$ ions are produced from chemical oxidation of *N*-alkylthioureas [27, 28] and *N,N'*-dialkylthioureas [39, 40].

Above results for *s*-TUs indicate that faradaic processes occur within rather comparable potential windows. The electroformation and electroreduction of dimers take place in the 0.05 to 0.9 V range, coupled to the electrodissolution of gold, although for the latter no direct evidence can be derived from the voltammograms. The formation of the oxygen adlayer on gold [34] and the further electro-oxidation of *s*-TUs and *s*-FDS undergo in the range 0.9 to 1.6 V.

Voltammetric electro-oxidation of adsorbed thioureas

Sulphur-containing molecules are prone to adsorb on metal electrodes through the S atom, the respective S-metal bond strength being moderately strong [41]. Accordingly, the voltammogram on gold scanned from 0.05 to 1.6 V involves

Fig. 1 Stabilised voltammograms of MTU, DMTU, ETU and DETU on gold electrode run at 0.05 V s^{-1} between 0.05 and 1.7 V, 1 mM TUs + 0.1 M perchloric acid, 298 K
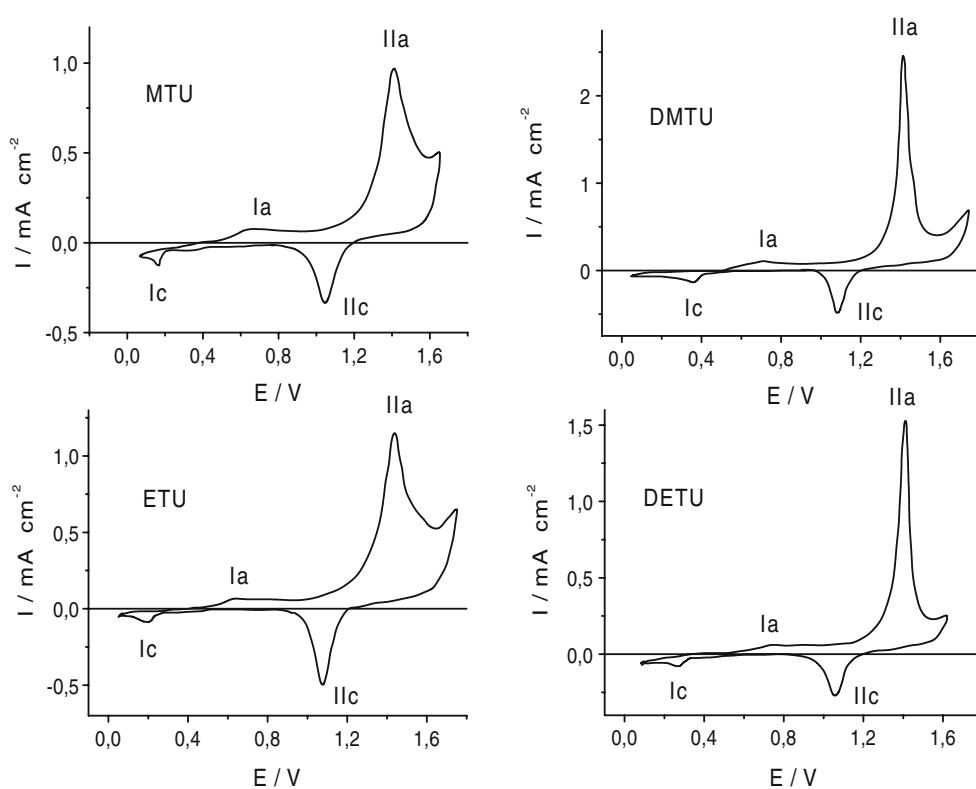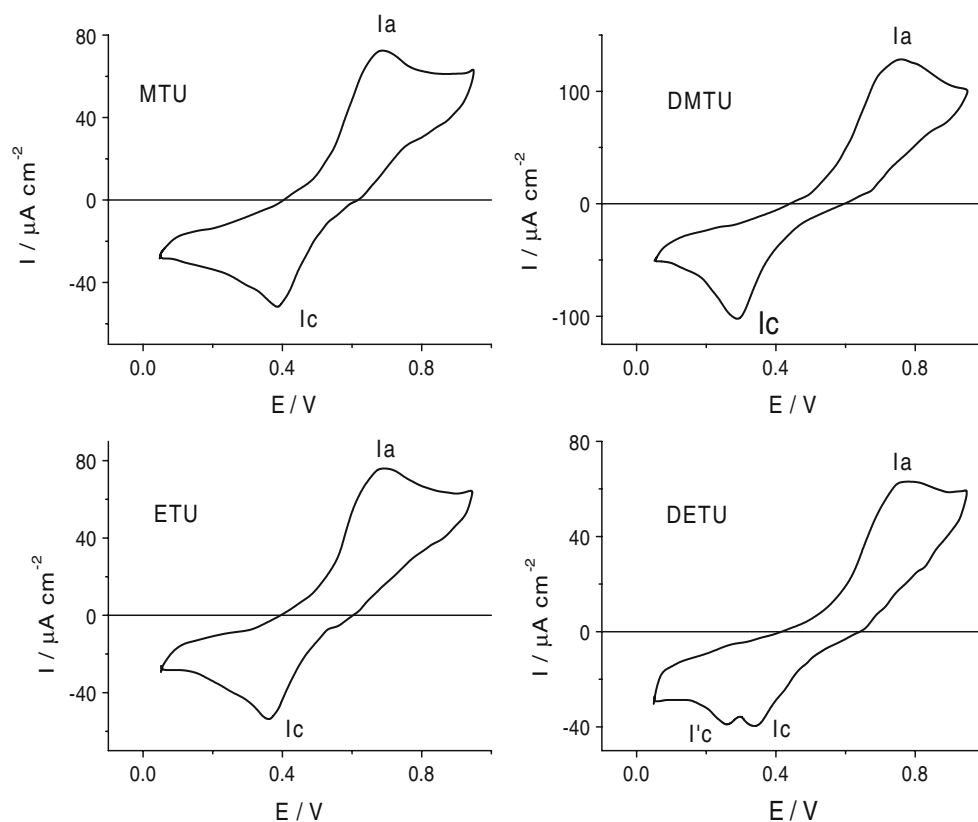
anodic currents from the electro-oxidation of both soluble and adsorbed TU and s-TU species and products from their adsorbate decomposition.

To investigate the presence and electro-oxidation of adsorbed s-TUs, the gold electrode was immersed in 0.1 mM s-TU + 0.1 M perchloric acid for 300 s at 0.05 V, transferred at constant potential to plain 0.1 M perchloric acid, and immediately a voltammogram from 0.05 to 1.7 V and backwards was run. For each s-TU, its voltammetric electro-oxidation takes place from about 1.3 upwards, although for MTU a small electro-oxidation current below 1.2 V is also recorded (Fig. 3). This is an indication that the electro-oxidation of the respective s-TU adsorbate mainly occurs in the second potential window without evidence for the respective disulphide formation. Seemingly, the kinetics of disulphide formation is rate determined by s-TU molecules coming from the solution side into the electrode–solution interface.

The voltammetric s-TU electro-oxidation to gold oxygen adlayer formation charge density ratio is 2.14 for MTU, 1.89 for DMTU, 1.76 for ETU and 1.65 for DETU. These figures were obtained from the first voltammetric electro-oxidation scan that involves about 90% of the adsorbate coverage for all s-TUs. The above charge ratio decreases on going from N-alkyl to N,N'-dialkyl thioureas, as expected from a decrease in the specific surface coverage with the increase of the size of the s-TU adsorbate.

FTIRRAS data

To identify the electro-oxidation products resulting from each s-TU and their dependence on the applied potential, in situ p- and s-polarised FTIRRAS spectra in the range 1,000–2,500 cm^{-1} for 0.05 V stepwise increase in E in the range 0.1–1.6 V were recorded. These spectra reflected changes in the concentration of soluble reactants and products in the thin solution layer produced by the electrochemical reaction.

The identification and assignment of infrared (IR) bands were made comparing data for each s-TU to those that are reported in the literature [8, 42–45]. A major problem arose with the identification of bands presumably related to the presence of soluble gold-s-TU complexes. To our best knowledge, no IR information on these compounds is available. Then, intending to overcome this drawback, IR spectra run in deuterium oxide were compared to those previously reported for TU and TMTU electro-oxidation on gold and platinum, as in contrast to gold, no platinum electrodissolution seemingly occurs.

Electro-oxidation of N- and N,N'-methyl-thiourea

The presence of an ill-defined bipolar bands at 1,556/1,593 cm^{-1} in the IR spectra of MTU confirms an incipient electro-oxidation at 0.4 V (Fig. 4). The appearance of

Fig. 3 Voltammograms of MTU, DMTU, ETU and DETU adsorbed on gold run at $v=0.05$ V s^{-1} between 0.05 and 1.7 V in 0.1 M perchloric acid. Thioureas were previously adsorbed by immersing the electrode at 0.05 V during 300 s in 0.1 mM TUs + 0.1 M perchloric acid. *Dotted line*: base voltammogram
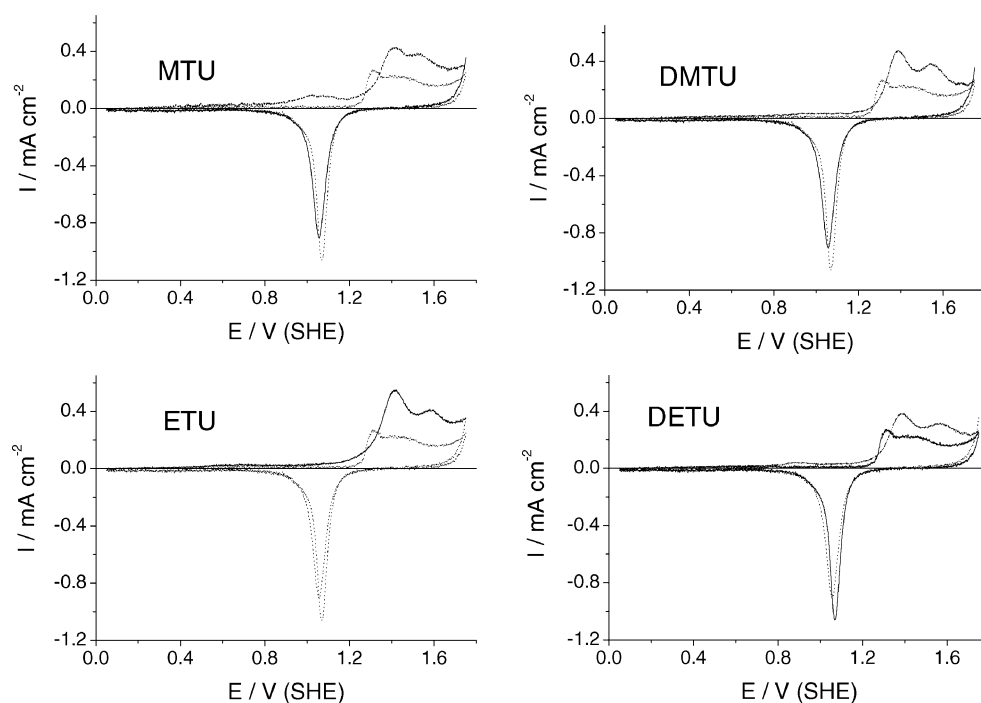
positive bands at 1,296; 1,398; 1,475 and 1,556 cm^{-1}, their intensities increasing with E, indicates the progressive depletion of MTU in the thin solution layer (Table 1). The band at 1,296 cm^{-1} can be assigned to the rocking of NH$_2$ groups and the stretching of the CS bond [42]. The bands at 1,398 cm^{-1} and 1,475 cm^{-1} are related to the symmetric bending and the bending and rocking of CH$_3$, respectively, and that at 1,556 cm^{-1} to the stretching of the CN bond.

Above positive bands occur simultaneously with negative bands at 1,108; 1,123; 1,321; 1,420; 1,589 and 1,656 cm^{-1}, their intensities gradually increasing with E as expected for the increase in the concentration of products at the thin solution layer. The band at 1,108 cm^{-1} is due to perchlorate ions from the base electrolyte. The bipolar band at 1,556/1,589 cm^{-1} indicates the depletion of MTU and the simultaneous formation of soluble gold–MTU complex. For the latter, the frequency increase of the NH deformation and CN antisymmetric stretching bands results from the fact that the MTU-gold atom coordination implies a decrease in the C=S double-bond character and an increase in the C–N single bond charge density to attain a double bond character. In general, ca. 15–30 cm^{-1} blue shifts have been reported for *s*-TU–metal ion coordination [8, 9, 45].

The negative band at 1,655 cm^{-1} in part is attributed to the bending of water molecule and, in part, to the disulphide asymmetric CN stretching, the latter being the main electro-oxidation product at potentials below 1.0 V [30, 32]. Further details about these bands are referred to in the following sections.

For $E=0.4$ V, the negative band at 1,589 cm^{-1}, in contrast to the negative band at 1,656 cm^{-1} from 0.45 V upwards, indicate that gold electrodissolution starts somewhat earlier than the proper electro-oxidation of MTU to disulphide.

From $E=1.05$ V upwards, the negative band at 2,228 cm^{-1} can tentatively be assigned to the C≡N stretching from cyanamide species. From $E=1.40$ V upwards, there are two new negative bands at 1,202 and 2,343 cm^{-1} the intensity of them increases with E. The former can be assigned to the O–S–O stretching from bisulphate ion, and the latter to the O–C–O asymmetric stretching from carbon dioxide [46]. Accordingly, at potentials sufficiently positive, cyanamide, carbon dioxide and sulphate ions appear in the thin solution layer.

As E is increased from 0.4 V upwards, the spectra of DMTU exhibit positive bands at 1,142; 1,301; 1,362; 1,463; 1,527 and 1,578 cm^{-1} (Fig. 4) indicating DMTU depletion at the thin solution layer. The band at 1,301 cm^{-1} can be assigned to the CS bond stretching; those at 1,362 cm^{-1} and 1,463 cm^{-1} to the bending of the CH$_3$ group; that at 1,437 cm^{-1} to the NH bending and CN stretching, and those at 1,527 and 1,578 cm^{-1} to the NH bending and CN stretching, respectively [43–45].

The negative bands that appear from $E=0.45$ V upwards indicate the gradual depletion of DMTU by the electro-oxidation process. The intensities of the negative bands at 1,090; 1,345; 1,421; 1,496; 1,554 and 1,603 cm^{-1} increase slightly with E. Following the criteria applied for interpreting the MTU spectra, the band at 1,554 cm^{-1} is assigned to the formation of a soluble gold–DMTU complex, and that at 1,603 cm^{-1} to the formation of the respective disulphide.

For $E=1.5$ V, the new negatives bands at 1,212 and 2,343 cm^{-1} indicate the increase in the concentration of

Fig. 4 *p*-Polarised FTIRRAS spectra of 0.1 M MTU and 0.1 M DMTU on gold in aqueous 0.1 M perchloric acid at different sampling potentials. E_{ref}=0.05 V
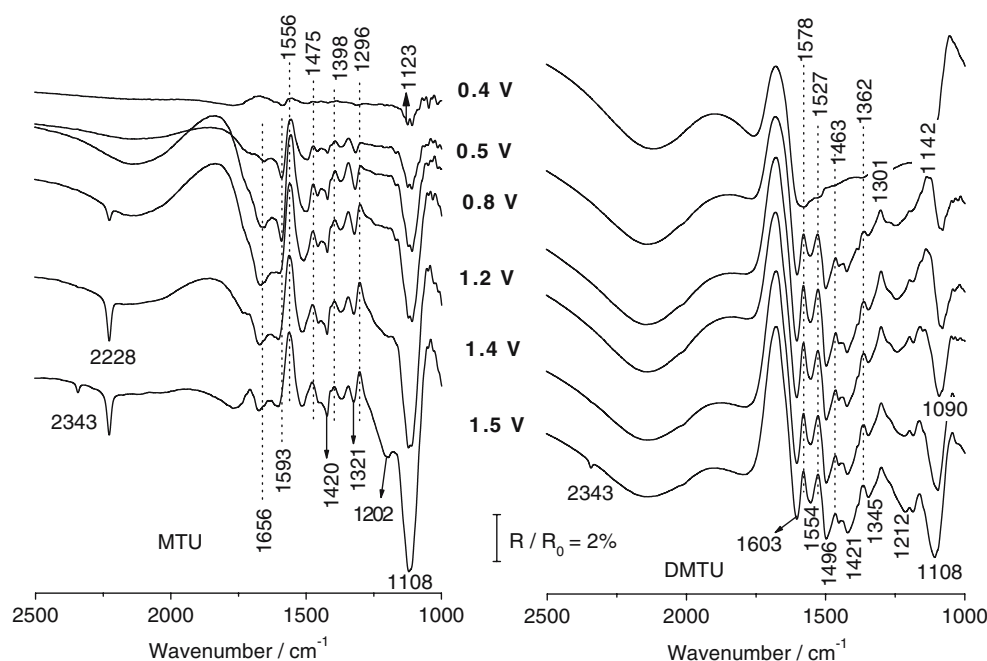
bisulphate ions and carbon dioxide in the thin solution layer.

Electro-oxidation of N- and N,N'-methyl-thiourea adsorbates

After MTU adsorption on gold at 0.05 V during 300 s from 0.1 M MTU + 0.1 M perchloric acid (Fig. 5), the FTIRRAS spectra in plain 0.1 M perchloric acid, for E=1.2 V, show negative bands at 1,200 and 2,228 cm^{-1}, and for E=1.5 V, similar bands at 1,200 and 2,343 cm^{-1}. Accordingly, for E< 1.5 V, adsorbed MTU on gold appears to be completely electro-oxidised to sulphate and cyanamide and to carbon dioxide and sulphate for E=1.5 V.

From E=1.2 V upwards, the spectra of DMTU adsorbates exhibit negative bands at 2,343 and 1,200 cm^{-1} indicating that carbon dioxide and bisulphate ions are formed. Two weak positive bands at 2,850 and 2,922 cm^{-1} that are assigned to the symmetric and asymmetric stretching of the CH bond, respectively, are also observed. These bands suggests that DMTU, at variance to TMTU [47], lies with its major molecular axis tilted with respect to the substrate plane. Furthermore, it should be noted that the negative band related to disulphide formation is not observed.

Electro-oxidation of N- and N,N'-methyl-thiourea in deuterium oxide

To exclude the interference of water bands preventing the identification of the formamidinium disulphide bands, FTIRRAS was run in deuterium oxide solutions.

From E=0.5 V upwards (Fig. 6), the spectra of MTU exhibit positive bands at 1,364; 1,401; 1,423 and 1,545 cm^{-1}, and negative ones at 1,378; 1,414; 1,439; 1,586 and 1,649 cm^{-1}. The band at 1,586 cm^{-1} appears for E=0.4 V, but is no longer observed for E=1.1 V. This band is similar to those found for both TU [37] and TMTU [32] electro-oxidation on gold that were assigned to the formation of a soluble gold–MTU complex. This band was not observed for those processes undergoing on platinum [30, 38].

The intensity of the negative band at 1,649 cm^{-1} increases with E. From the comparison to the spectra of products from both TU [37] and TMTU [32] electro-oxidation on gold in deuterium oxide, and to the IR spectrum of the [TMTU]$^{2+}$ recently reported [32] that band is assigned to the CN$_2$ asymmetric stretching of the respective disulphide. As E approaches 1.5 V, the band intensity at 1,586 cm^{-1} decreases in contrast to that at 1,649 cm^{-1}. These facts indicate that the MTU–gold complex is electro-oxidised to the respective disulphide at this potential.

The intensity of the negative band at 1,244 cm^{-1} increases with the concentration of sulphate ions at the thin solution layer assisted by migration.

A similar FTIRRAS behaviour is observed for DMTU (Fig. 6). In this case positive bands at 1,384; 1,413; 1,443 and 1,545 cm^{-1} and negative bands at 1,107; 1,180; 1,260; 1,396; 1,584 and 1,642 cm^{-1} are recorded. The negative band at 1,584 cm^{-1} is tentatively assigned to a soluble gold–DMTU complex and that at 1,642 cm^{-1} to the respective disulphide.

Negative bands at 1,110; 1,180 and 1,260 cm^{-1} point out the increasing concentration of sulphate/bisulphate ions

Fig. 5 *p*-Polarised FTIRRAS spectra at different sampling potentials of the electro-oxidation of MTU and DMTU adsorbed on gold during 300 s at 0.05 V. 0.1 M perchloric acid. E_{ref}=0.05 V
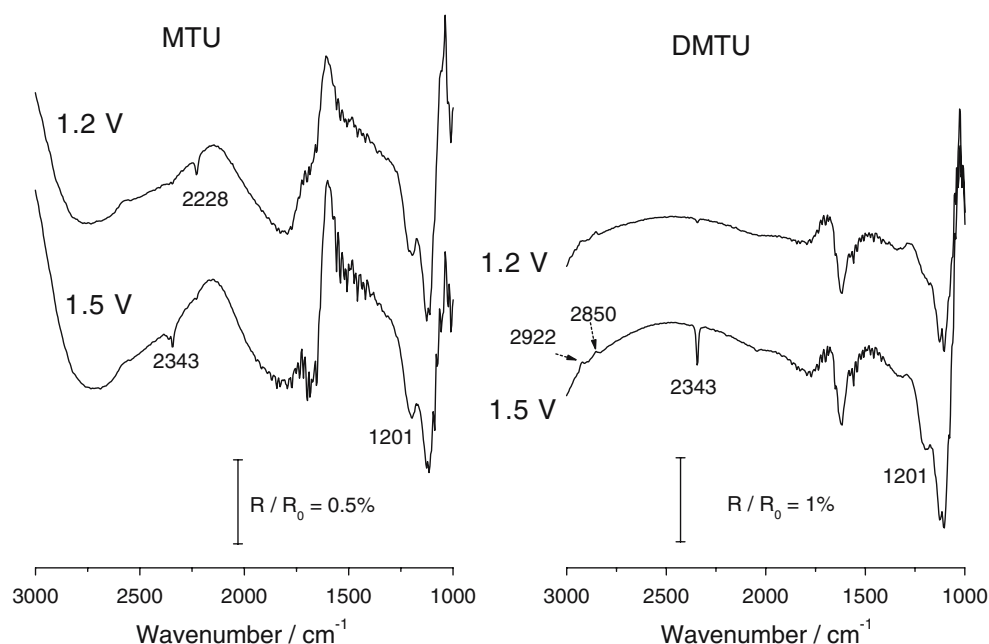
from both the base electrolyte solution and the electro-oxidation of *s*-TU at the thin solution layer.

Electro-oxidation of N- and N,N'-ethyl-thiourea

The *p*-polarised FTIRRAS spectra of ETU and DETU along their electro-oxidation from 0.45 V upwards show a gradual depletion of *s*-TU in the thin solution layer (Fig. 7). For ETU, setting the baseline spectrum at 0.4 V, the positive bands at 1,274; 1,351 and 1,548 cm^{-1} agree with those reported for solid ETU (Table 2). The band at 1,351 cm^{-1} is assigned to the CH_3 torsion and CH_2 wagging and that at 1,547 cm^{-1} to the CN and CS stretching and the NCN bending (Table 2). The NH_2 bending band expected at ca. 1,636 cm^{-1} is probably obscured by the respective water band.

Out of the negative bands at 1,311; 1,501; 1,586 and 1,610 cm^{-1}, those at 1,586 and 1,610 cm^{-1}, largely overlapped, can only be detected for $E<1.0$ V. These bands are also considerably influenced by the absorption bands of water (Fig. 7). Seemingly, as for MTU and DMTU, in this case the spectra of ETU and DETU reveal the formation of the respective disulphide (band at 1,610 cm^{-1}) and soluble gold–ETU complex (band at 1,586 cm^{-1}), which are more extensively described further on.
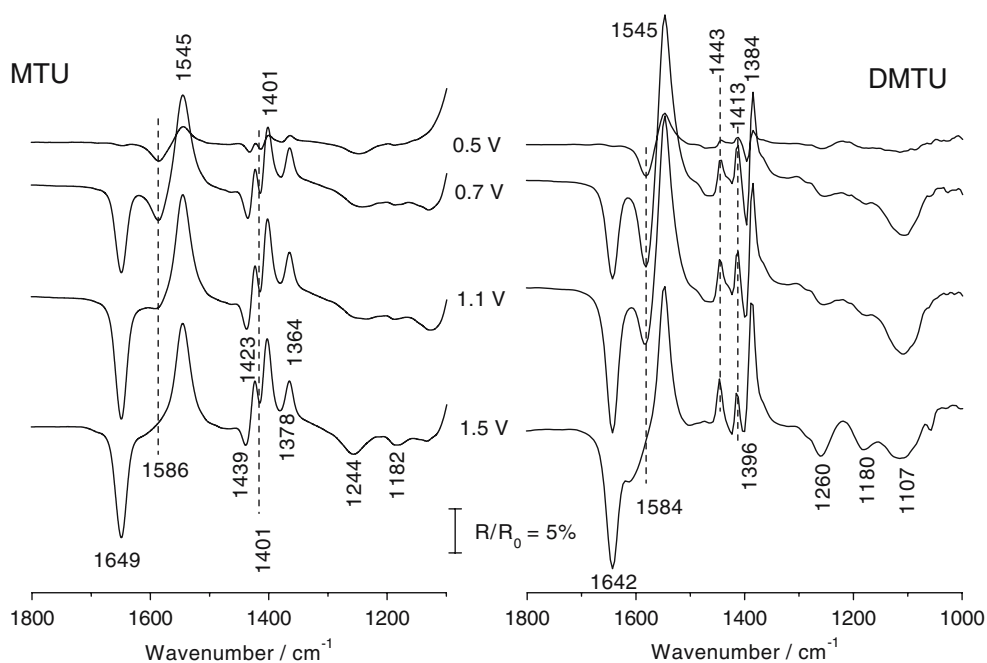
For $E>1.3$ V, similar to MTU (see above), new negative bands at 1,204 and 2,224 cm^{-1}, due to the formation of bisulphate and cyanamide, are found. For $E=1.5$ V, a small negative feature at 2,343 cm^{-1} seems to indicate carbon dioxide formation in the thin solution layer.

On the other hand, for $0.5 \leq E \leq 1.3$ V the spectra of DETU show rather intense positive bands at 1,301; 1,396; 1,526 and 1,570 cm^{-1} and weaker ones at 1,458 and 1,480 cm^{-1}, all related to the depletion of DETU. Among the negative bands at 1,276; 1,445; 1,497; 1,544; 1,594 and 1,620 cm^{-1}, the latter is also present for $E=0.1$ V, i.e., a potential where no electro-oxidation of DETU occurs. Because of it, the band at 1,620 cm^{-1} that can tentatively be assigned to water would mask negative bands in this wave number range that would presumably be related to electro-oxidation products from DETU.

The bands at 1,594 cm^{-1} and 1,497 cm^{-1} exhibit the same *E*-dependent intensity. In principle, they can be assigned to the formation of a soluble gold–DETU complex.

For $E=1.5$ V, the negative band at 1,200 cm^{-1} is due to bisulphate ion formation and the small feature at 2,343 cm^{-1} to the incipient formation of carbon dioxide. As for ETU, carbon dioxide formation is less important. In this case, at variance with ETU, no cyanamide absorption band can be

Table 1 Principal infrared bands of MTU and DMTU

MTU [43]		DMTU [44, 45]	
Wave number/cm^{-1}	Assignment	Wave number/cm^{-1}	Assignment
1,124s	νNCH_3,	1,038	δNCN, νCN
1,149s	$\delta_r CH_3$	1,082	ρCH_3
1,258w	δNH	1,287	νCS
1,297vs	δNH, νCN	1,358	δCH_3
1,404s	$\delta_s CH_3$	1,420	δNH, νCN
1,454s	$\delta_a CH_{-3}$	1,446	δCH_3
1,489s	δNH, νCN	1,506	νCS, δNH
1,556vs	νCN, δNH	1,568	νCN, δNH
1,627s	δNH_2		
1,637s	δNH_2		

detected. It seems that the presence of CH_3 groups on both N atoms prevents the formation of C≡N bonds.

Electro-oxidation of N- and N,N'-ethyl-thiourea adsorbates

From 1.2 V upwards, the FTIRRAS spectra of products from adsorbed ETU electro-oxidation on gold show a small negative feature at 1,200 cm^{-1} and a negative band at 2,224 cm^{-1} due to bisulphate ions and cyanamide formation, respectively (Fig. 8). When E is increased to 1.5 V, the

negative band at 2,343 cm^{-1} from carbon dioxide formation and the weak positive bands at 2,850 and 2,930 cm^{-1} due to the disappearance of methyl groups, are recorded.

On the other hand, for adsorbed DETU the FTIRRAS spectra exhibit negative bands at 1,200 and 2,343 cm^{-1}. No band related to the C≡N stretching is found. This indicates that the adsorbate electro-oxidation yields directly carbon dioxide and bisulphate ions. These spectra also exhibit positive bands at 2,850 and 2,930 cm^{-1} related to the stretching of the CH bond of methyl groups. These bands
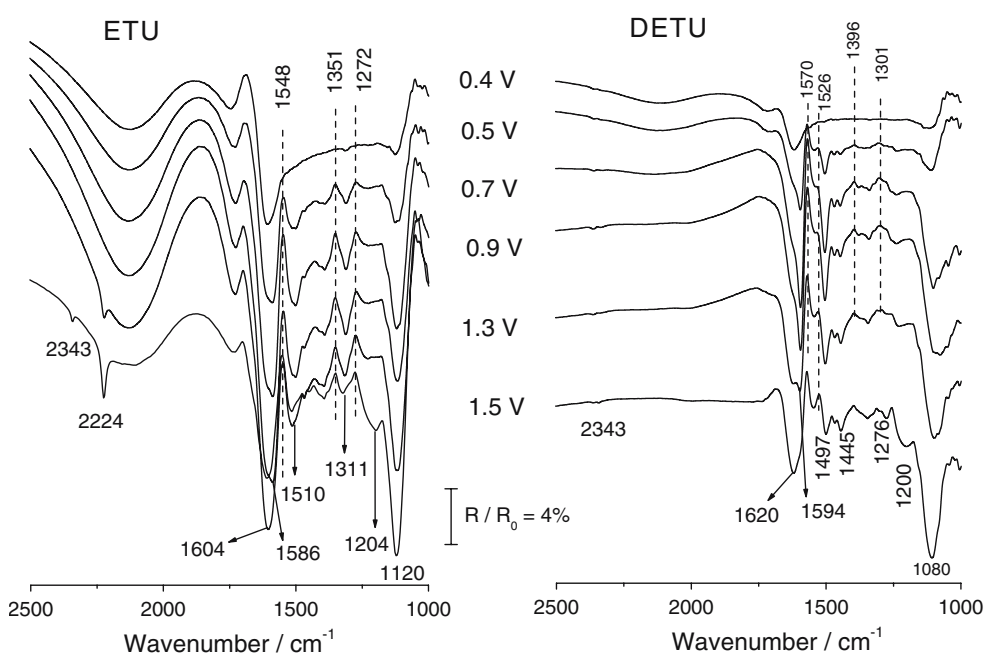
Table 2 Principal infrared bands of ETU and DETU

ETU [46]		DETU [44]	
Wave number / cm^{-1}	Assignment	Wave number / cm^{-1}	Assignment
1,110s	νCN	1,063	ν_sCN, δNCN
1,263s		1,091	ρ CH$_3$
1,347m	τ CH$_3$, ωCH$_2$	1,288	δNCS, νCS
1,498m	νCN	1,340	δCH$_3$
1,543vs	νCN, δNCN, νCS	1,384	δNH, ν_aCN
1,562s	νCN, δNCN, νCS	1,457	δCH$_3$
1,636vs	δNH$_2$	1,499	δNH
2,855s	ν_sCH$_2$	1,553	ν_aCN, δNH
2,927s	ν_aCH$_2$		

become more intense and better defined for DETU than for other s-TU, probably because of the proper localisation and specific orientation of DETU adsorbates on gold.

Electro-oxidation of N- an N,N'-ethyl-thiourea in deuterium oxide

The FTIRRAS spectra of ETU dissolved in deuterium oxide run from E=0.5 V upwards show positive bands at 1,380; 1,403 and 1,530 cm^{-1}, and negative bands at 1,108; 1,194; 1,256; 1,426; 1,577 and 1,641 cm^{-1} (Fig. 9). While the negative band at 1,577 cm^{-1} appears already for E= 0.4 V, those at 1,641 and 1,108 cm^{-1} are observed from E= 0.5 V upwards. From the comparison of these results to those reported for gold and platinum [30, 32, 38], it is reasonable to assign the band at 1,641 cm^{-1} to the formation of the respective disulphide, and that at 1,577 cm^{-1} to soluble gold–ETU complex.

Accordingly, gold electrodissolution in ETU-containing solutions precedes the electro-oxidation of ETU to its respective disulphide. The latter tends to dominate the overall reaction as E is increased. The intensity of the negatives bands at 1,423 cm^{-1} and 1,577 cm^{-1} increase as E is gradually changed from 0.4 to 0.7 V and then decrease. These bands should be related to the presence of the gold–ETU complex in the thin solution layer. The band at 1,423 cm^{-1} is still visible in the spectra even when the negative band at 1,577 cm^{-1} has already disappeared. At sufficiently high values of E, the band at 1,577 cm^{-1} is likely masked by the strong intensity of the positive band at 1,530 cm^{-1} related to the depletion of ETU at the thin solution layer.

FTIRRAS spectra of DETU dissolved in deuterium oxide run from E=0.4 V upwards show positive bands at 1,237; 1,403; 1,448 and 1,531 cm^{-1} and negative bands at

1,120; 1,182; 1,426; 1,567 and 1,630 cm^{-1} (Fig. 9). The pair of bipolar bands 1,403/1,426 and 1,531/1,567 cm^{-1} can be related to the depletion of DETU and the simultaneous formation of soluble gold–DETU complex in the thin solution layer. The former process occurs at 0.5 V where no disulphide is produced yet. In fact, the intensity of the positive bands at 1,403 and 1,531 cm^{-1}, smaller than those at 1,426 and 1,567 cm^{-1}, is consistent with the fact that DETU depletion turns out to be low at lower E, but increases as both the gold complex and the respective disulphide are simultaneously formed. Furthermore, the wave number difference of ca. 12 and 35 cm^{-1} in the bipolar bands agrees with the formation of a gold–thiourea complex [22]. This band blue shift results from the metal–sulphur bonding that increases the electron density of the CN bond [9].

Discussion

Voltammograms of the N-alkyl and N,N'-dialkyl thioureas in aqueous acid solutions on polycrystalline gold run from 0.05 to 1.6 V at 0.05 V s^{-1} exhibit comparable faradaic reactions occurring in almost similar ranges of potentials. At low potentials (peaks I_a/I_c) the adsorption of s-TU, the electrodissolution of gold yielding the respective gold soluble complex and the electroformation of the respective disulphides are dominant processes.

At higher potentials (peak II_a), the electro-oxidation of the respective s-TU adsorbate and disulphide yielding cyanamide, carbon dioxide and sulphate ions, followed by the subsequent formation of O-containing adlayer on gold take place.

Adsorbates from N-alkyl and N,N'-dialkyl thiourea

Seemingly, the electrochemical behaviour of s-TU does not differ greatly from that of TU. In acidic solutions TU molecules are in equilibrium with thiouronium cations [48]

$$SC(NH_2)_2 + H_3O^+ \rightleftharpoons HSC(NH_2)_2^+ + H_2O \qquad (2)$$
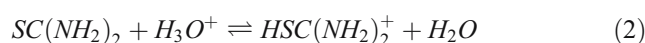
although the pK_a value reported in the literatura (pK=1.44 [49], pK=3.5 [48]) indicates that the percentage of thiouronium ions should be low for a 0.1–0.5 M acid concentration. In this case, the equilibrium of TU with its canonical form

$$SC(NH_2)_2 \rightleftharpoons HSC(NH_2)_2 \qquad (3)$$

appears to be more important. The adsorption of the canonical TU form yields the canonical radical (*SC(NH) NH$_2$) that bears a negative charge giving rise to a thiourate anion, its surface bonding capability being similar to that of alkanethiols [48]. According to recent XPS data the energy

window of the S_{2p} peak of TU on Ag (111) coincides with that for alkanethiolates [50]. Similarly, STM imaging of TU, S and ETU adsorbates on Ag (111) provided further evidence of TU adsorption via the canonical TU radical [50].

On the other hand, canonical TU can also be electro-adsorbed via a fast electron and proton transfer reaction that can be detected, for instance, by triangular modulated voltammetry [32],
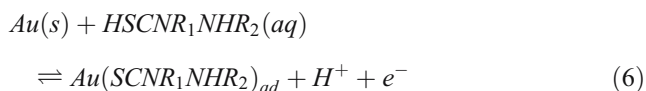
$$Au + HSC(NH)(NH_2)(aq)$$
$$\rightleftharpoons Au(SC(NH)(NH_2))_{ad} + H^+ + e^- \qquad (4)$$
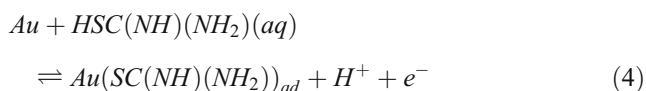
Analogous behaviours are feasible for partially substituted thiourea, as in principle these s-TU are also in equilibrium with their respective canonical form, making these molecules easily adsorbable via a gold–sulphur bond [13, 14]. In fact, both voltammetry and FTIRRAS data indicate that N-alkyl and N,N'-dialkyl-thioureas readily form stable adsorbates in aqueous acid in the range 0.05 to ca. 1.2 V. The IR active symmetric and asymmetric CH stretching bands in the FTIRRAS spectra (Figs. 5 and 8) indicate the likely non-dissociative adsorption of these s-TU molecules on gold surface. In contrast to TMTU that lies flat on the metal (111) surfaces [51], these adsorbates acquire upright tilted positions with respect to the substrate plane. This conclusion from spectra is consistent with theoretical calculations of TU adsorbate structures on platinum and silver single crystal surfaces [48]. It has been demonstrated that although in the absence of electric field the most stable adsorption geometry is that of flat TU, for sufficiently positive electric fields, the upright configuration coordinated via the S atom becomes the preferred one [48]. Therefore, both the electro-oxidation and electrodissolution reactions are preceded by the spontaneous adsorption of reactantes. The coverage of gold surface by s-TU adsorbates, as derived from the respective voltammetric electro-oxidation charge (Fig. 3), is of the order of 10^{-10} mol cm^{-2}.

Accordingly, the initial interaction between s-TU and gold surface can be written either,

$$2Au(s) + HSCNR_1NHR_2(aq)$$
$$\rightleftharpoons Au(SCNR_1NHR_2^*)_{ad} + H^+ + e^-(Au) \qquad (5)$$
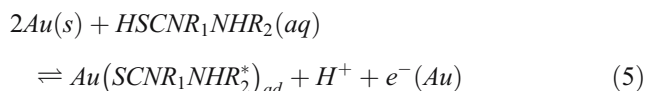
yielding the radical adsorbate denoted by the asterisk.or

$$Au(s) + HSCNR_1NHR_2(aq)$$
$$\rightleftharpoons Au(SCNR_1NHR_2)_{ad} + H^+ + e^- \qquad (6)$$

where for N-alkyl-thioureas R_1 and R_2 stand for CH$_3$ or C$_2$H$_5$ and H, respectively, whereas for N,N'-dialkyl-thioureas, R_1 and R_2 denote for CH$_3$ or C$_2$H$_5$.

Both electrosorption reactions involve a Au–S bond formation similarly to other organosulphur adsorption processes reported for gold and silver [52].

Reaction (5) occurs under open circuit and changes the distribution of electrical charge at the interface. In the presence of molecular oxygen, reaction (5) is coupled to the electroreduction of dioxygen, the global reaction being

$$O_2 + Au(SCNR_1NHR_2^*)_{ad} + 2e^-(Au) + 4H^+$$
$$\rightarrow 2H_2O + 2Au(s) + Au(SCNR_1NHR_2^*)_{ad} \qquad (7)$$
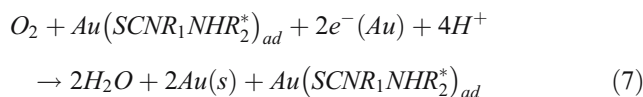
Reaction (6), which competes with reaction (5), dominates as E is increased. It favours the electrodissolution of gold as a gold–s-TU soluble complex. Thus, upon adsorption the length of the SC bond of the canonical s-TU considerably increases, and the CN bond length becomes intermediate between that of a single and the double bond [48] because of the increase in the electron density of the CN$_2$ bond. The negatively charged adsorbate likely induces a protonation of the adsorbate in contact with the acid solution,

$$Au(SCNR_1NHR_2^*)_{ad} + H^+$$
$$\rightleftharpoons [Au(SCNHR_1NHR_2)_{ad}]^+ \qquad (8)$$
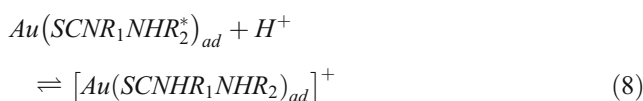
the product from reaction (8) likely acts as a precursor for the electrodissolution of gold in acid solutions.

As E is positively shifted the enlargement of the SC bond of the adsorbate eventually results in the appearance of S atoms and C-containing surface residues. In fact, STM images of TU on gold (111) in going from 0.4 to 1.0 V, have shown adsorbate pattern structure transitions from TU to FDS adsorbate, and eventually to S octomers [53].

For s-TU, as for TU, the relatively strong S–Au surface interaction would also favour the formation of disulphide adsorbate via two neighbour adsorbates,

$$2Au_n(SCNR_1NHR_2)_{ad} \rightarrow [Au_{2n}(SCNR_1NHR_2)_2]_{ad} \qquad (9)$$
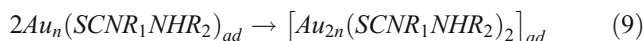
although it should be noted that quantum mechanical calculations indicate that surface disulphides are prone to dissociate into their respective monomers [48, 54].

Spectral data reveals that as E is increased, the S–Au bond strength also increases and the disulphide adsorbate likely decomposes leaving adsorbed S atoms and CN-containing residues. For $E \geq 1.2$ V sulphur atoms are electro-oxidised to sulphate ions and CN-containing residues to either cyanamide or/and carbon dioxide (Figs. 5 and 8).

Electrochemical processes in the range 0.4–1.0 V

The first electro-oxidation threshold potential of N-alkyl and N,N'-dialkyl thioureas (peak I_a) is close to that reported for TU on gold [36]. Conversely, for s-TU solutions,

Fig. 8 *p*-Polarised FTIRRAS spectra of 0.1 M ETU and 0.1 M DETU on gold in aqueous 0.1 M perchloric acid at different sampling potentials. E_{ref}=0.05 V
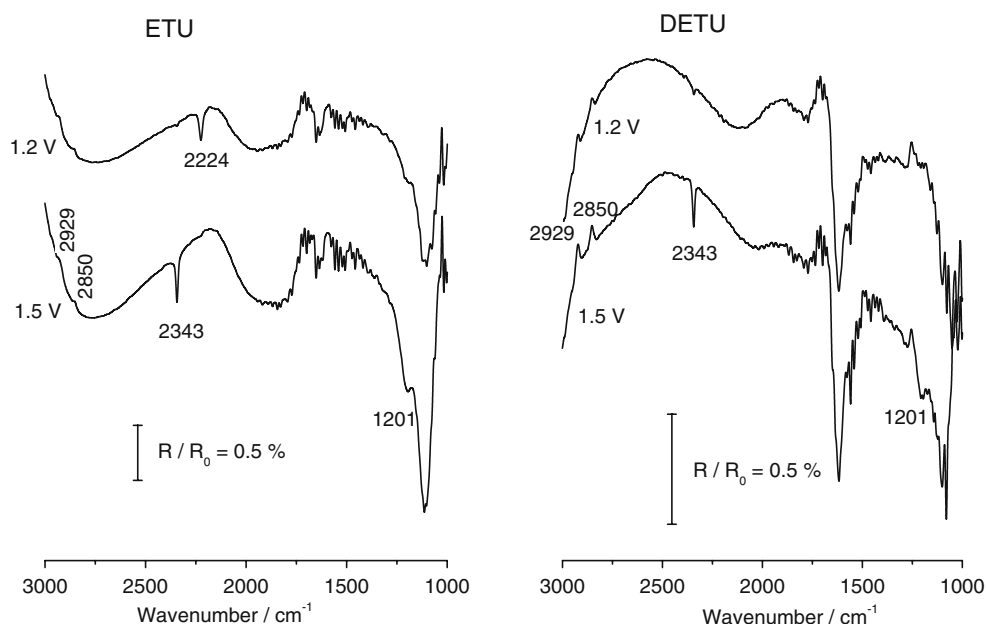

FTIRRAS data from 0.4 V upwards indicate the formation of both soluble *s*-TU-gold complexes and disulphides. Seemingly, the electrodissolution of gold precedes the formation of disulphides albeit both reactions proceed simultaneously from 0.5 V upwards. FTIRRAS bands indicating the depletion of *s*-TU in the thin solution layer are recorded from ca. 0.45 V upwards, irrespective of *s*-TU. The first negative band at 1,560–1,590 cm^{-1} is coherent with the appearance of a soluble CN-containing product, its spectrum being characterised by a CN stretching band blue-shifted by the electron density increase in the CN$_2$ bond that results from the formation of the S–Au bond.

At E=0.5 V, once the electrodissolution of gold sets in, the band at 1,600–1,650 cm^{-1} reveals the formation of the respective disulphide. This is consistent with both FTIRRAS data from *s*-TU dissolved in deuterium dioxide, and data previously reported for the electro-oxidation of TU [37] and TMTU [32]. The formation of a disulphide salt is consistent with the fact that thiols are readily oxidised to disulphides. In neutral or weakly acidic medium, the disulphide ion spontaneously decomposes with the precipitation of sulphur.
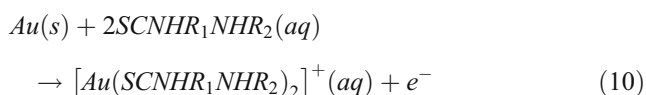
For all *s*-TU, the mean potential value resulting from peaks I_a and I_c is ca. 0.5 V (Fig. 2), a value close to the reversible potentials of several thiourea–disulphide redox

Fig. 9 *p*-Polarised FTIRRAS spectra of 0.1 M ETU and 0.1 M DETU on gold in 0.1 M sulphuric acid deuterium oxide at different sampling potentials. E_{ref}=0.05 V
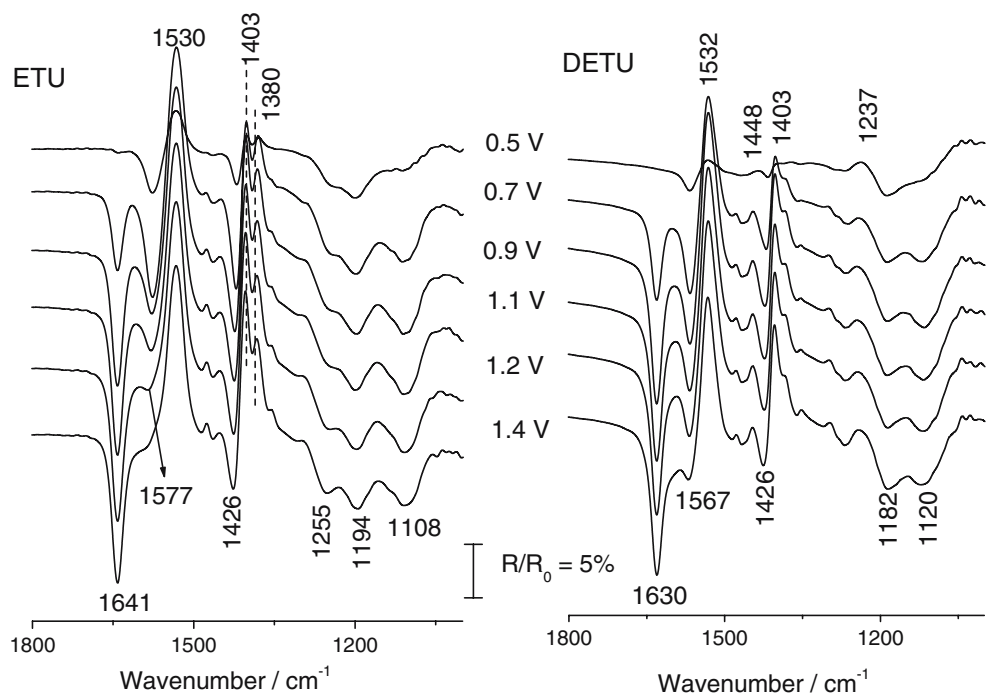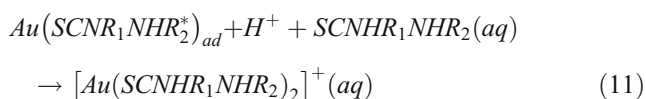
couples [39]: $E° = 0.42$ V (TU), 0.46 V (MTU) and 0.45 V (DETU). Besides, the potential difference between peaks I_a and I_c is higher than 0.030 V, the value expected for a two-electron conjugated electrochemical reaction. This difference indicates a rather sluggish kinetics of the first electro-oxidation stage for all s-TUs. The kinetics of disulphide formation involves a mass-transport control from the solution side and an electron transfer at an electrode surface partially blocked by adsorbates [36, 55].

Therefore, the first electro-oxidation stage should include the interaction between s-TU and gold yielding s-TU–Au soluble complex,
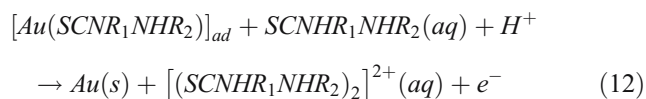
$$Au(s) + 2SCNHR_1NHR_2(aq)$$
$$\rightarrow \left[Au(SCNHR_1NHR_2)_2\right]^+ (aq) + e^- \quad (10)$$

The same product can also be produced via adsorbed species,

$$Au\left(SCNR_1NHR_2^*\right)_{ad} + H^+ + SCNHR_1NHR_2(aq)$$
$$\rightarrow \left[Au(SCNHR_1NHR_2)_2\right]^+ (aq) \quad (11)$$

Reactions 10 and 11 assume that the number of ligands per complex molecule is 2, in agreement with the structure of Au–TU complexes reported in the literature [56]. Unfortunately, for alkyl and di-alkyl thiourea–gold complexes no structure date were found.

Both voltammetry (Fig. 2) and FTIRRAS data (Figs. 4 and 7), indicate that along with gold electrodissolution the formation of disulphide (peak I_a) occurs. As flow cell FTIRRAS spectra show no evidence of disulphide formation from s-TU adsorbate electro-oxidation, soluble disulphides are more likely produced either from s-TU in solution and s-TU adsorbates, i.e.

$$\left[Au(SCNR_1NHR_2)\right]_{ad} + SCNHR_1NHR_2(aq) + H^+$$
$$\rightarrow Au(s) + \left[(SCNHR_1NHR_2)_2\right]^{2+}(aq) + e^- \quad (12)$$

or from two s-TU molecules in solution

$$2SCNHR_1NHR_2(aq) \rightarrow \left[(SCNHR_1NHR_2)2\right]^{2+}(aq) + 2e^-$$
$$(13)$$

Reactions 12 and 13 proceed under a diffusion controlled kinetics interfered by the presence of adsorbates partially blocking the gold electrode surface.

Electrochemical processes in the range 1.0–1.6 V

For $E > 1.0$ V (peak II_a) the electro-oxidation of both adsorbate and soluble compounds formed at $E < 1.0$ V, and the formation of O-containing adlayer at the gold available free sites take place.

The respective FTIRRAS data indicate at least three electro-oxidation products, i.e. cyanamide, carbon dioxide and sulphate ions produced from both adsorbates and soluble s-TU derived species. At 1.4 V the electro-oxidation of S atoms to aqueous sulphate [57] is confirmed by the appearance of the O–S–O stretching band at 1,200 cm^{-1}. The sulphate band that appears at ca. 1,050–1,100 cm^{-1} is masked by the symmetric stretching band of perchlorate that appears at 1,100 cm^{-1}.

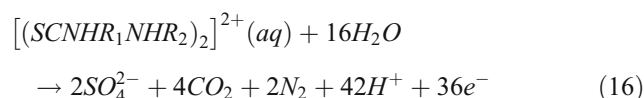Sulphate ions can be formed from residual S atoms adsorbed on the gold surface,

$$S(s) + 4H_2O \rightarrow SO_4^{2-}(aq) + 8H^+(aq) + 6e^- \quad (14)$$
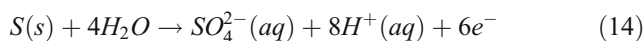
participating in the following equilibrium in acid solution

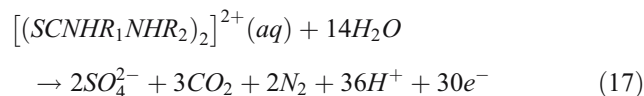$$SO_4^{2-}(aq) + H^+(aq) \rightleftharpoons HSO_4^-(aq) \quad (15)$$
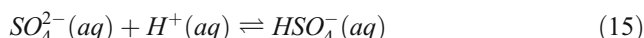
This reaction explains the appearance of the bisulphate absorption band at ca. 1,200 cm^{-1}.

On the other hand, sulphate ions are also produced from complete electro-oxidation of s-TU disulphides

$$\left[(SCNHR_1NHR_2)_2\right]^{2+}(aq) + 16H_2O$$
$$\rightarrow 2SO_4^{2-} + 4CO_2 + 2N_2 + 42H^+ + 36e^- \quad (16)$$

for $R_1 = H$, $R_2 = C_2H_5$ or $R_1 = R_2 = CH_3$ or

$$\left[(SCNHR_1NHR_2)_2\right]^{2+}(aq) + 14H_2O$$
$$\rightarrow 2SO_4^{2-} + 3CO_2 + 2N_2 + 36H^+ + 30e^- \quad (17)$$

for $R_1 = H$, $R_2 = CH_3$ or

$$\left[(SCNHR_1NHR_2)_2\right]^{2+}(aq) + 20H_2O$$
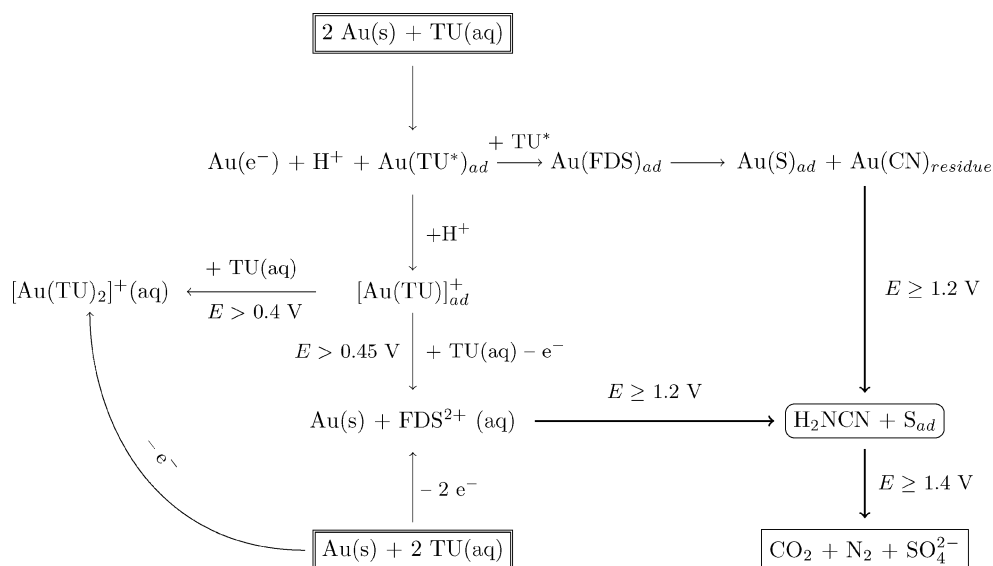$$\rightarrow 2SO_4^{2-} + 6CO_2 + 2N_2 + 54H^+ + 48e^- \quad (18)$$
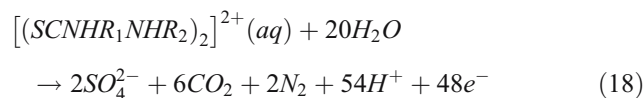
for $R_1 = R_2 = C_2H_5$

The formation of N_2 has been detected by DEMS from the electro-oxidation of TU on gold [58] and platinum [38].

The complete electro-oxidation of s-TU disulphides, either adsorbed or in solution, starts at 1.2 V yielding, according to FTIRRAS data, both carbon dioxide and sulphate ions. The formation of these products is likely assisted by O-adlayers on gold for $E > 1.3$ V.

In contrast to N,N'-dialkyl thioureas, the complete electro-oxidation of N-alkyl thioureas is preceded by the formation of C≡N-containing species, most likely cyanamide, as revealed by the band in the 2,200–2,250 cm^{-1} region, the wave number range of C≡N stretching band [46]. Cyanamide is a major product in the oxygen-assisted oxidative degradation of TU [59, 60] and C≡N bands have been detected by in situ FTIRRAS during the electro-oxidation of TU on gold [37] and platinum [30, 38, 61]. As expected, N-alkyl adsorbates also yield cyanamide previous to carbon dioxide formation.

Fig. 10 General reaction scheme for the electroadsorption and electro-oxidation of TU and N-substituted TU on gold. FDS stands for their respective disulphides

$$2\,\mathrm{Au(s)} + \mathrm{TU(aq)}$$

$$\mathrm{Au(e^-)} + \mathrm{H^+} + \mathrm{Au(TU^*)}_{ad} \xrightarrow{+\ \mathrm{TU^*}} \mathrm{Au(FDS)}_{ad} \longrightarrow \mathrm{Au(S)}_{ad} + \mathrm{Au(CN)}_{residue}$$

$$[\mathrm{Au(TU)_2}]^+(\mathrm{aq}) \xleftarrow[E > 0.4\ \mathrm{V}]{+\ \mathrm{TU(aq)}} [\mathrm{Au(TU)}]^+_{ad}$$

$+\mathrm{H^+}$

$E > 0.45\ \mathrm{V}\ \big|\ +\ \mathrm{TU(aq)} - \mathrm{e^-}$

$E \geq 1.2\ \mathrm{V}$

$$\mathrm{Au(s)} + \mathrm{FDS^{2+}}\ (\mathrm{aq}) \xrightarrow{E \geq 1.2\ \mathrm{V}} \boxed{\mathrm{H_2NCN} + \mathrm{S}_{ad}}$$

$-2\ \mathrm{e^-}$

$E \geq 1.4\ \mathrm{V}$

$$\mathrm{Au(s)} + 2\,\mathrm{TU(aq)}$$

$$\mathrm{CO_2} + \mathrm{N_2} + \mathrm{SO_4^{2-}}$$

Based on results from combined FTIRRAS and voltammetry for s-TU on gold and electro-oxidation data that have been reported for TU and TMTU on gold and platinum, it is possible to advance a general scheme for the adsorption and electro-oxidation of TU and N-substituted thioureas (Fig. 10) and N,N'-substituted thioureas (Fig. 11) on gold. The reaction pathway involves a relatively fast adsorption of these molecules via radical adsorbates. The latter, at low potentials, i.e. 0.4 V, yields a gold–s-TU soluble complex by a single electron transfer reaction per adsorbate. As E is increased, the positively charged adsorbate reacts with a second molecule, yielding the respective disulphide in solution by a subsequent single electron transfer reaction. For TU and N-substituted thioureas and $E > 1.2$ V, both adsorbate and disulphide species are first electro-oxidised to cyanamide and later to carbon dioxide and sulphate ions
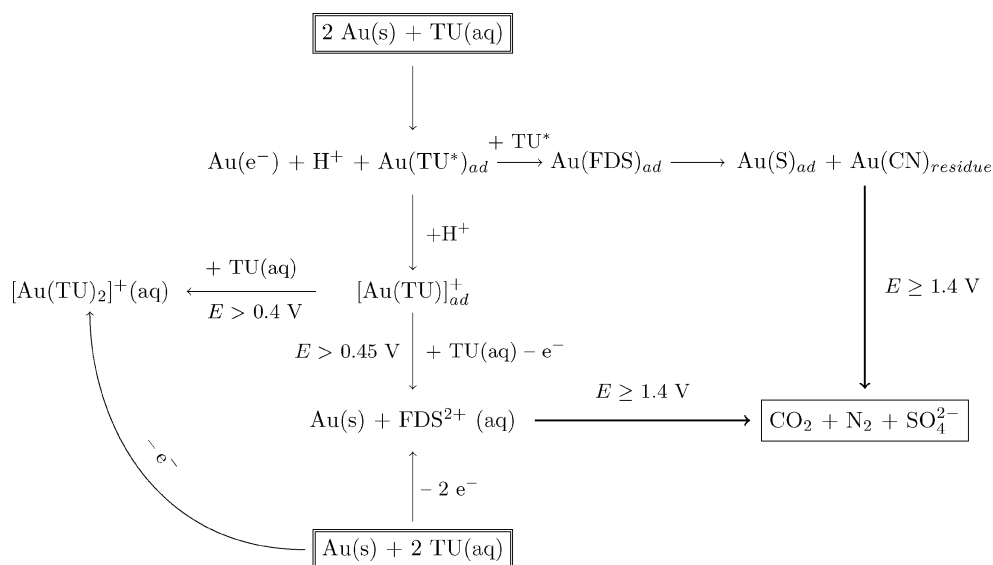
(Fig. 10), i.e. this occurs for those s-TU that have at least one free amine group.

On the other hand, when both amine groups are partially (DMTU, DETU) or full substituted (TMTU), they are electro-oxidised directly to carbon dioxide and sulphate ions for $E > 1.4$ V (Fig. 11). These reaction pathways can also be extended for platinum electrodes [30, 38], omitting those reactions involving the formation of soluble complex species.

Conclusions

(1) Both N-alkyl and N,N'-dialkyl thioureas are readily adsorbed on polycrystalline gold electrodes for $E < 1.2$ V in acid solution. These adsorbates participate in

Fig. 11 General reaction scheme for the electroadsorption and electro-oxidation of N, N'-substituted thioureas (TU) on gold. FDS stands for the respective disulphides

$$2\,\mathrm{Au(s)} + \mathrm{TU(aq)}$$

$$\mathrm{Au(e^-)} + \mathrm{H^+} + \mathrm{Au(TU^*)}_{ad} \xrightarrow{+\ \mathrm{TU^*}} \mathrm{Au(FDS)}_{ad} \longrightarrow \mathrm{Au(S)}_{ad} + \mathrm{Au(CN)}_{residue}$$

$$[\mathrm{Au(TU)_2}]^+(\mathrm{aq}) \xleftarrow[E > 0.4\ \mathrm{V}]{+\ \mathrm{TU(aq)}} [\mathrm{Au(TU)}]^+_{ad}$$

$+\mathrm{H^+}$

$E > 0.45\ \mathrm{V}\ \big|\ +\ \mathrm{TU(aq)} - \mathrm{e^-}$

$E \geq 1.4\ \mathrm{V}$

$$\mathrm{Au(s)} + \mathrm{FDS^{2+}}\ (\mathrm{aq}) \xrightarrow{E \geq 1.4\ \mathrm{V}} \boxed{\mathrm{CO_2} + \mathrm{N_2} + \mathrm{SO_4^{2-}}}$$

$-2\ \mathrm{e^-}$

$$\mathrm{Au(s)} + 2\,\mathrm{TU(aq)}$$

subsequent electrodissolution and electro-oxidation processes that take place on the partially covered gold surface.

(2) From 0.5 to 1.0 V the electrodissolution of gold by s-TU as a gold–s-TU complex in solution precedes the voltammetric electro-oxidations of N-alkyl and N,N'-dialkyl thioureas that produce the respective disulphides.

(3) From 1.0 V upwards, the electro-oxidation of s-TU adsorbates and s-TU disulphides takes place yielding soluble products such as sulphate ions, carbon dioxide and cyanamide, their relative yield depends on the type of thiourea considered. The electro-oxidation of thiourea competes with the formation of the oxygen-containing layer on gold.

(4) At least one non-substituted amine group should exist in s-TU molecules to produce cyanamide as electro-oxidation product, as the presence of alkyl groups prevents the formation of C≡N bonds.

(5) A general reaction pathway for the adsorption and electro-oxidation of thioureas on noble metal electrodes can be advanced considering the participation of adsorbates and molecules in solution that participate in the formation of several electro-oxidation products.

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