Electrochemical Behavior of Some Substituted Thiosemicarbazones and their Reaction Products with Tetracyanoethylene

S.A.M. Refaey, A.A. Hassan and H.S. Shehata

Chemistry Department, Faculty of Science, Minia University, Minia, Egypt.
*E-mail: saeed_refaey@hotmail.com

The electrochemical behavior of substituted thiosemicarbazones has been investigated. It is found that the cyclic voltammetry of all substitutions is different; this can be attributed to the nature of terminal aldehydic group. Also the electrochemical behavior of reaction products of substituted thiosemicarbazones with tetracyanoethylene (TCNE) have been investigated by cyclic voltammetry.

1. INTRODUCTION

Oxidation of aldehyde semicarbazone and thiosemicarbazone derivatives by metal salts has been used for the synthesis of 1,2,4-triazole, 1,3,4-oxadiazole and 1,2,4-thiadiazole derivatives [1-6]. Different reagents such as bromine, hypobromite, bromate [7,8], iodate, and high valence transition metal salts have been used to perform these reactions. [1, 2, 5, 9, 10].On other occasions, the cyclization mechanism involves a plain oxidation step-electron abstraction or dehydrogenation prior to the actual ring closure step. [11-13].

The electrochemical reduction of 2-formylpyridine thiosemicarbazone has been studied. The reduction is an irreversible process since no peak is observed in the positive sweep. Kitaev et al [14] and Lund [15, 16] have been reported that the reduction of aromatic thiosemicarbazones should occur through the transfer of 4 electrons: the cleavage of N-N single bond by reduction with 2 electrons and then reduction by 2 electrons at the imine formed [17]. The oxidation and reduction of these compounds was studied by polarography and coulometric measurements in order to correlate the structure with the biological activity [18]. Thiosemicarbazones have been widely used as photometric

ligands, especially in determination of traces of transition metals [19]. The redox properties of some thiosemicarbazones and their metal complexes have been studied [20, 28].

Pyridine-*n*-aldehyde thiosemicarbazones have been used to modify gold electrode [29-30]. The authors suggested that the interaction with surface occurs via sulphur and perhaps imine nitrogen [31]. Substitutions of thiosemicarbazones in the 2 position of the pyridine ring are reduced at more negative potentials than the other isomers due to the intramolecular hydrogen bonding [32].

The aim of the present study is focused on the redox behavior of substituted thiosemicarbazones and the influence of these substitutions in the thiosemicarbazone moiety on the redox properties. One purpose of this study is the electrochemical behavior of the products from the reactions of substituted thiosemicarbazones and ethenetetracarbonitrile (TCNE). Ethenetetracarbonitrile is the simplest of percyanoalkenes (cyano-carbon) [33]. It is an electron-deficient substance due to the presence of dicyanovinylidene moiety. TCNE is known to form stable charge transfer complexes when reacted with suitable electron-rich derivatives [34].

2. EXPERIMENTAL PART

The 1,4-thiosemicabazone derivatives were prepared by condensation of phenyl thiosemicarbazones with appropriate aldehyde according to the references [35-39]. The working electrode was pt electrode of 0.125 cm^{-2} in the form of rod welded to Cu wire for electrical connection. This form is fixed in glass tube, and the platinum rod was covered by small sphere of glass at the end .The electrode must rinse in acetone, distilled water, and finally with acetone before using. The counter electrode was also pt-electrode with the same area. The reference electrode was calomel electrode. The solution contains 1,4-thiosemicabazone, tetrethylammonium perchlorate (Fluka), and acetonitril as solvent. The solution deaerated by nitrogen bubbling. The cell (pyrex glass) used has five openings in the main joint of the vessel, three of them for the three electrodes, and the other two as inlet and the outlet of the gas .The cell was of the double walled with tow opening for the circulation of the thermostat water. The electrochemical behavior of 1,4-thiosemicabazone was accomplished in acetonitrile solution of 0.1 M of (Et)$_4$NClO$_4$ and 0.01 M of 1,4-thiosemicabazone using CV technique, in the potential range –2200-2200 mV and scan rate (100-1000 mVs^{-1}). The CV curves were recorded by a potentiostate (AMEL model 2049), which was PC-controlled.

3. RESULTS AND DISCUSSION

3.1. The electrochemical behavior of substituted thiosemicarbazones:

The cyclic voltammogram of substituted phenylthiosemicarbazones (scheme 1) were investigated at the potential range (-2100 to 2200 mV) and the voltammetric data are collected in table (1). Figure (1) shows the cyclic voltammogram of 4-phenyl thiosemicarbazide (1). It shows two anodic peaks and two cathodic peaks were prepared by condensation of compound 1 with aromatic and heterocyclic aldehydes (scheme 1). This reaction is a type of protection of amino function by aldehydic

group [40]. The cyclic voltammogram of aldehyde thiosemicarbazones (2a-2g) are different than that of 4-phenylthiosemicabazide (1) and most of them display three anodic peaks and three cathodic peaks. The electrochemical process is irreversible due to the peak-to-peak potential separation is large.
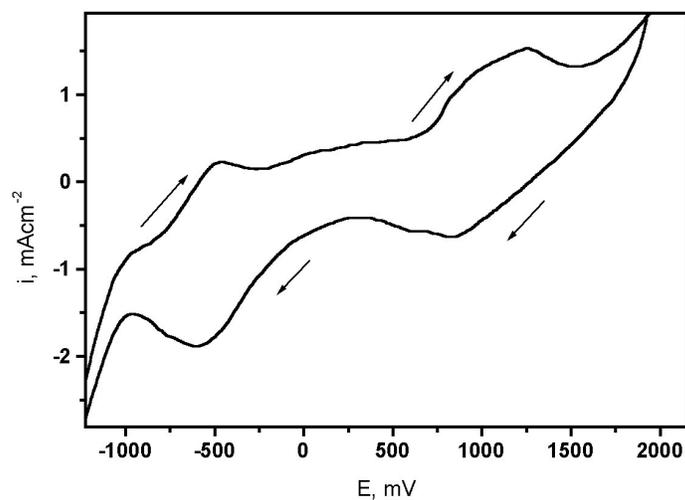

R: a= C_6H_5, b= C_6H_4Cl-*P*, c= $C_6H_4OCH_3$-*P*, d= C_6H_4OH-*O*, e= $C_6H_4N(CH_3)_2$, f= C_4H_4S, g= C_4H_4O
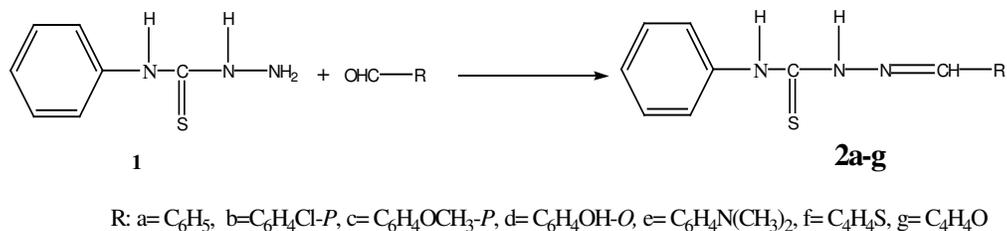
Scheme 1.

Figure 1. Cyclic voltammogram of 0.01 M 4-phenythiosemicrabazide (1) in a solution of 0.1 M $(Et)_4NClO_4$ / acetonitril at scan rate 500 mVs^{-1} .
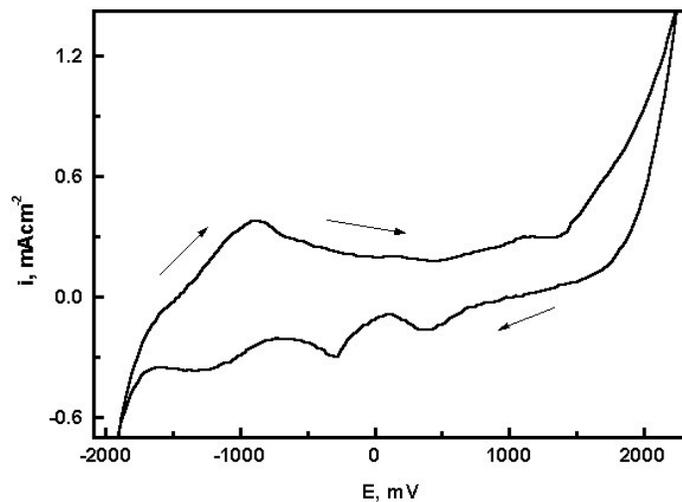

Figure 2. Cyclic voltammogram of 1-benzyledine-4- thiosemicarbazide (2a) in a solution of 0.1 M $(Et)_4NClO_4$ / acetonitril at scan rate 500 mVs^{-1} .

The electrochemical behavior of compound (1) is more different than its derivatives due to the absence of NH_2 and the attachment of the aldehydic group with the 4-phenylthiosemicarbazone. The addition of benzaldehydic group to the molecular framework leads to appearing new peaks, disappearing old peaks, and shift of some original peaks to more positive value as shown in fig. (2). By comparing the current peak height of compound (1) and compounds (2a-2g), it was found that the current peak height of compound (1) is higher than for compounds (2a-2g). This indicates that the stability of compound (1) is higher and the rate of reaction is faster due to the presence of free amino group. In compounds (2a-2g) the reactive amino group was blocked by many subsistuents. This view is in agreement with previous studies on the reaction of both compound 1 and compounds (2a-g) as donors with the acceptors [41, 42].
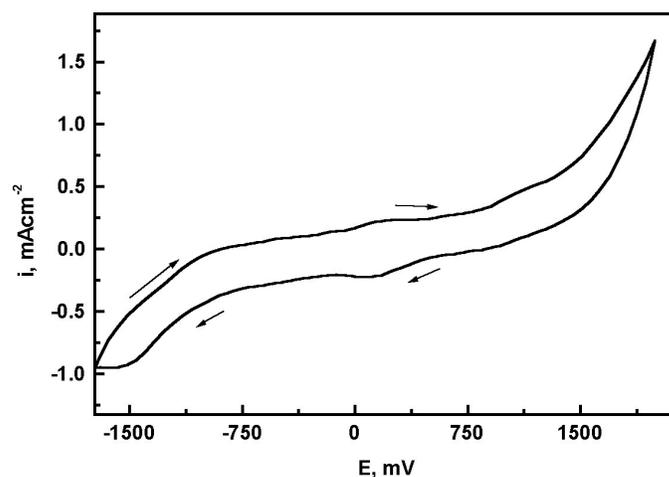

Figure 3. Cyclic voltammogram of 1-(4-chlorobenzylidene)-4-phenylthiosemicarbazide (2b) in a solution of 0.1 M $(Et)_4NClO_4$ / acetonitril at scan rate 500 mVs^{-1} .
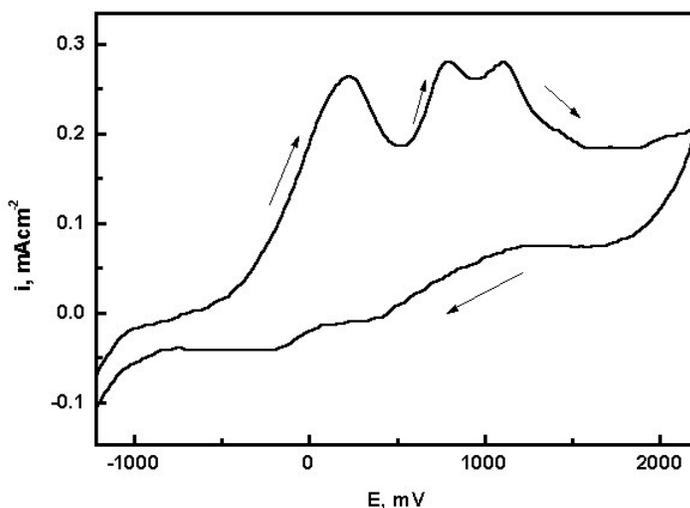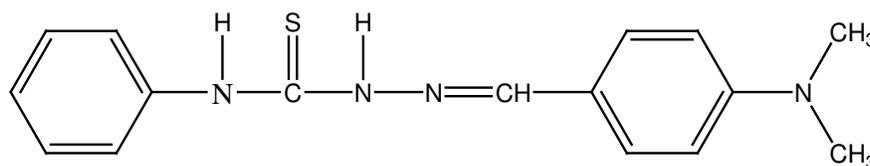

Figure 4. Cyclic voltammogram of compound1-(4-methoxybenzylidene)-4-phenylthiosemicarbazide (2c) in a solution of 0.1 M $(Et)_4NClO_4$ / acetonitril at scan rate 500 mVs^{-1}.

The electrochemical behavior of phenyl substituent of thiosemicarbazone (2a) is different than that for all other subsituents (2b-2g) as a result of the non electroactive characterization of phenyl group. The electron withdrawing groups such as C_6H_5 in (2a) or p-C_6H_4Cl in (2b) stabilize the compound; this appears from the reversibility of the first redox peaks. This is possible because the electron-withdrawing caused by chlorine or phenyl group makes a compound more positively charged, i.e., more easily reduced. The stability of a compound increases by increasing the withdrawing character (C_6H_4Cl-p > C_6H_5) (fig.3). Table (1) indicates the electrochemical behavior of both p-methoxy in (2c) and o-hydroxy in (2d) have similar electrochemical behavior due to the effect of these substituents as donating groups. This means that the compounds (2c, 2d) becomes easier to oxidize where electron donating groups increase the electron density at the reduction centers i.e. the compounds are more easily to oxidize [22]. The data in fig. 4 (as example) indicates that the adding of donor groups to compound (2a) increases the height of the oxidation peaks and leads to decay the cathodic peak height [43].
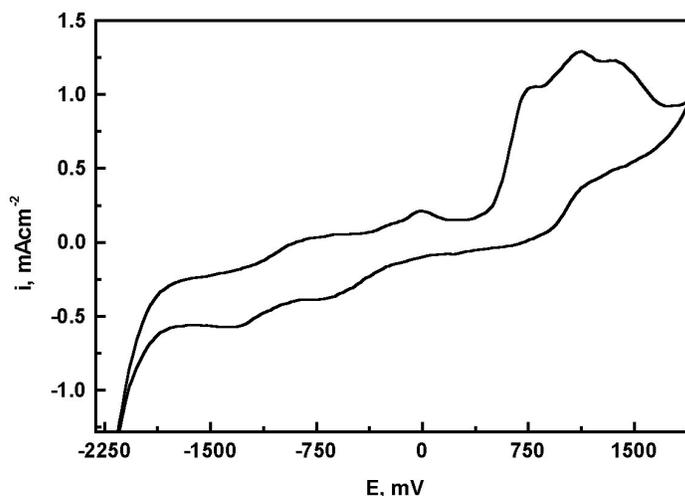

Scheme 2. (compound 2e)

Figure 5. Cyclic voltammogram of compound 1 - (4 - (dimethyl - amino) benzylidene) – 4 - phenylthiosemicarbazide (2d) in a solution of 0.1 M $(Et)_4NClO_4$ / acetonitril at scan rate 500 mVs^{-1} .

The cyclic voltammogram of 1-(4-(dimethyaminobenzylidene)-4-phenyl thiosemicarbazone (Scheme 2, Fig. 5) is a different and complicated than the last compounds. This difference can be attributed to the steric effect of the two-methyl groups which hindering the approach of the reduction center to the electrode surface [44]. The appearance of anodic peaks at the more positive values can be

attributed to a subsequent oxidation of the dication. Waltman et. al. [45] were studied the influence of geometric distortion on redox properties, they found that the distortion leads to shift of the reduction potentials to more negative values. By comparing the current peak heights for compound (2e) and other substituents, it is found that current peak heights for compound (2e) is the higher one due to the increasing of its donating character.

Table 1. Redox potentials of compounds 1 and 2(a-f) vs. SCE

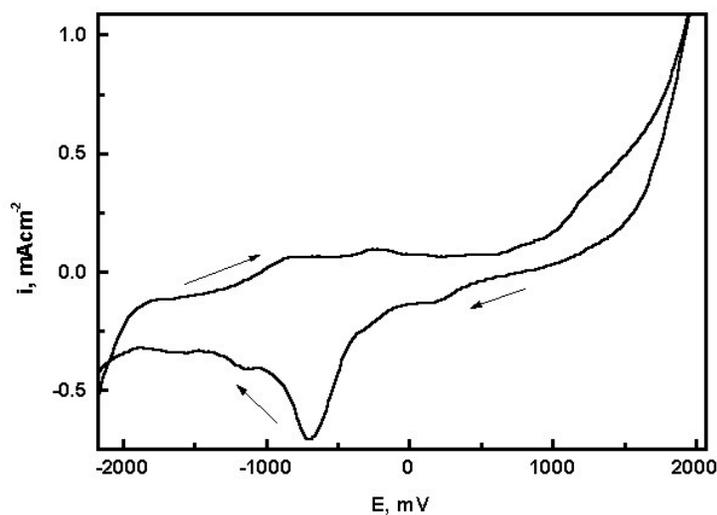| Compound	Epa1	Epa2	Epa3	Epa4	Epc1	Epc2	Epc3	Epc4
1	-476	1262	----	----	-590	824	----	----
2a	-896	145	1128	----	-1309	-287	376	----
2b	160	----	----	----	-1420	233	----	----
2c	224	789	1125	----	-230	365	1671	----
2d	255	648	1337	----	-212	212	1698	----
2e	-779	-21	768	1117-1373	-1365	-798	----	----
2f	-871	-235	-----	------	-1580	-1157	-703	175
2g	72	481	1024	----	-834	-157	196	----

Figure 6. Cyclic voltammogram of compound 4 – phenyl – 1 - ((thiophen - 2yl) methylene) thiosemicabazide (2f) in a solution of 0.1 M $(Et)_4NClO_4$ / acetonitril at scan rate 500 mVs^{-1}.

Replacing the phenyl group in compound (2a) by thiopheneyl (2f) or furfuraly (2g) groups, gives a different electrochemical behavior. The comparison between figure (6) and figure (7) indicates that the replacement of sulpher atom by oxygen atom leads to lowering both the anodic and cathodic current values; a similar behavior was obtained [46]. The presence of oxygen in the ring leads to shift the potential peak to the more positive values; on the other hand the presence of sulpher enhances the

reduction process (table 1). The presence of heterocyclic substitutes in compounds (2f, 2g) give a decrease of anodic current peaks related to the aromatic substitutes (2a-2e), this may be attributed to the increasing of conjugation in heterocyclic compounds, i.e. increase the reduction of the active groups. The aromaticty of thiophen ring is higher than that for furan ring due to the degree of participating of the oxygen lone pair in the aromatic sextet is less. The comparison of the compound 2f with thiophen itself, it is found that the attachment a chain to thiophen ring lowers the oxidation potential [47].
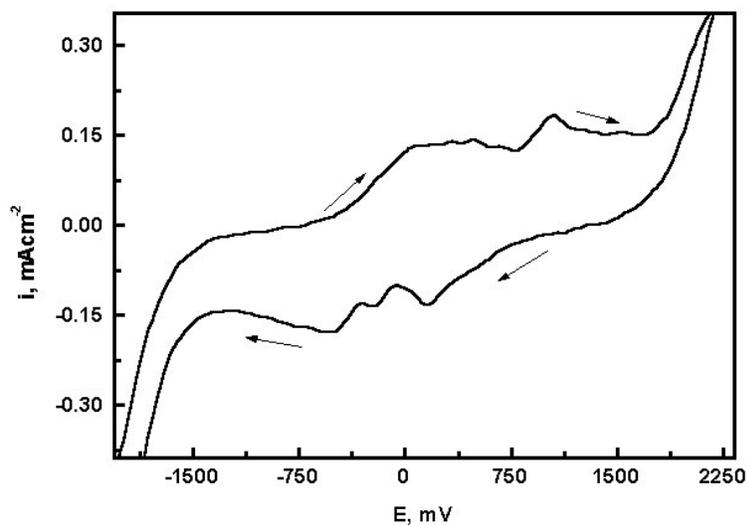

Figure 7. Cyclic voltammogram of compound 1-((furan-2-yl)-4-phenyl thiosemicarbazide (2g) in a solution of 0.1 M (Et)$_4$NClO$_4$ / acetonitril at scan rate 500 mVs^{-1}.
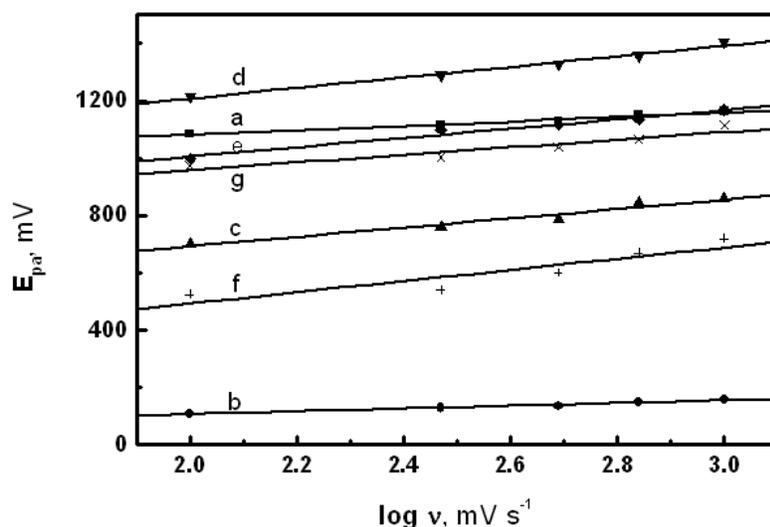

Figure 8. The dependence of E$_{pa}$ on log υ for 0.1 M of compounds (2a-2g) at platinum electrode surface.

By comparing the 4-phenylthiosemicarbazide (1) with the substituted 4-phenyl thiosemicarbazones (2a-2e), it is found that the degree of the irreversibility increases especially in the

case of the electrodonating groups. The degree of irreversibility is in the order [$C_6H_4N(CH_3)_2$ > C_6H_4OH > $C_6H_4OCH_3$ > C_6H_5 > C_6H_4 *p*-Cl]. The irreversible nature of these compounds makes them useful in the analytical applications [48]. Figure 8 (as example) indicates a linear relationship between anodic peak potential (E_{pa}) and scan rate. The results indicate that increasing the scan rate shifts the potential peaks to more positive direction, i.e. decrease the stability of compound. This supports the irreversibility of these compounds. It was observed that the potential difference ΔE_p increases with increasing scan rate; this indicates that the concentration of redox species cannot establish at the surface of the electrode according to the Nernest equation.
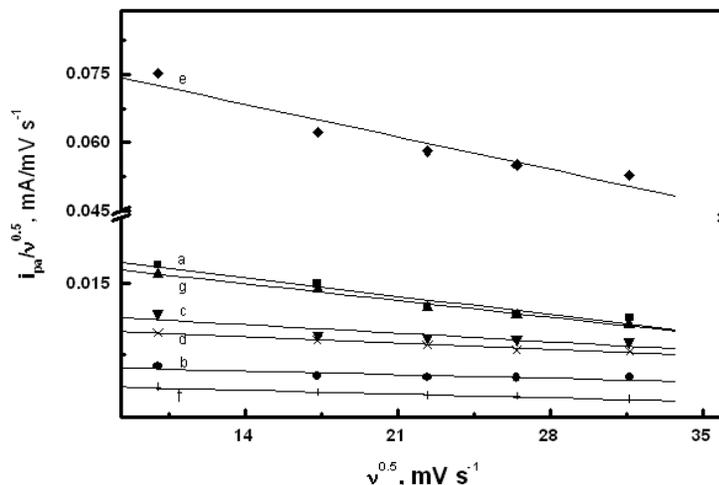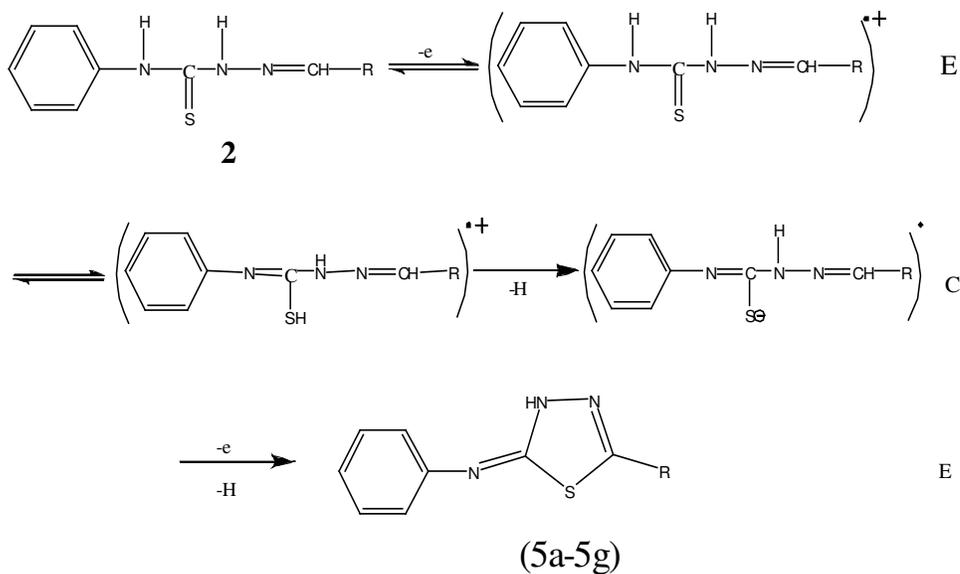

Figure 9. The dependence of the ratio ($i_{pa}/\upsilon^{1/2}$)on the square route of the scan rate (υ) for 0.1 M of compounds (2a-2g).
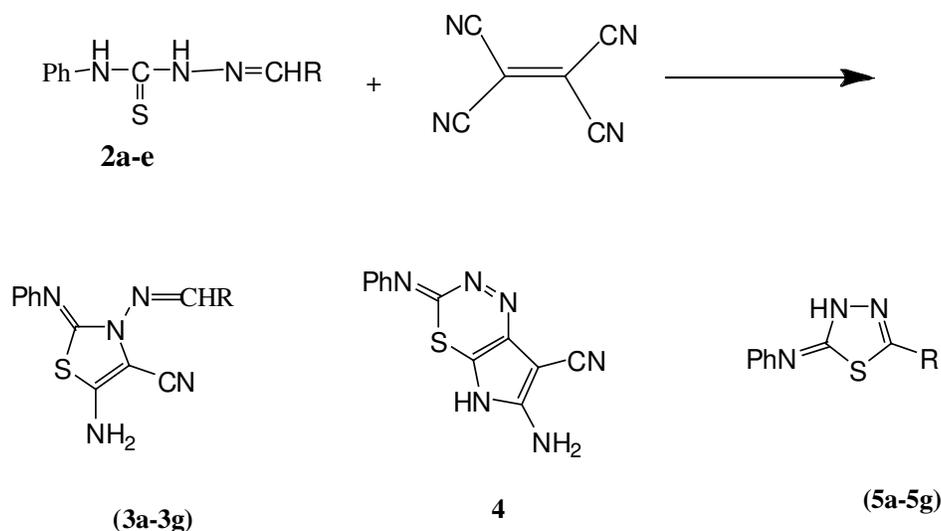

Scheme 3.

The dependence of the voltammetric response of compounds (2a-2g) on the scan rate is typical to an ECE mechanism (chemical reaction coupled between two charge transfer processes) [44-46]. The last results indicate that $i_{pc}/\upsilon^{1/2}$ decrease with increasing scan rate as suggested by Nicholson and Shain [49]. The dependence of the peak current on the square route of the scan rate ($\upsilon^{1/2}$) suggests diffusion-controlled electrochemical process (Fig. 9). Diffusion controlled means that the electron transfer from the organic compound to the electrode surface is much faster than the mass transfer to the surface of the electrode. One can suggest the mechanism of the electrochemical oxidation of the substituted 4-phenylthiosemicarbazones as follow in scheme (3).

The oxidation of thiosemicarbazones (2a-2g) generating cation radical is followed by a chemical reaction between cation radical and the residual water present in the medium. The resulting adduct undergoes the abstraction of the second electron to form thiadiazoles (5a-5g)

3.2. The electrochemical behavior of the products of reaction between 2a-2g with TCNE:

The reaction of compounds (2a-2e) with two molar equivalents of TCNE in ethyl acetate as solvent at room temperature produced the compounds 3, 4, and 5 [42] as shown in scheme (4).

4, 5 , 6	R
a	C_6H_5
b	$CH_3O\text{-}C_6H_4\text{-}p$
c	$Cl\text{-}C_6H_4\text{-}p$
d	$HO\text{-}C_6H_4\text{-}o$
e	$(CH_3)_2N\text{-}C_6H_4\text{-}p$

Scheme 4.

The cyclic voltammogrm of some compounds (3a, 4, and 5a) was studied as a representative compounds (figs. 10-12). The cyclic voltammogram of these compounds was run in the potential range (-500 to 2100 mV) and scan rate 500 mV s^{-1}. Fig 10 shows three anodic peaks and five cathodic peaks. The first anodic peak is reversible ($\Delta E_p = 65$ mV) and the third peak is quasi-reversible ($\Delta E_p = 102$ mV). The multi cathodic peaks can be attributed to the subsequent reduction of the formed radical anions. By comparing the voltammeric data of the produced compounds (3a, 4,and 5a) with compound (2a), it is found that the electrochemical behavior of each compound (3a, 5a) is similar to that of compound 2a (Tables 1 and 2). This result may be to the presence of R-CH=N- group in compounds (2a, 3a, 5a) and disappearance of this group in compound (4). The data in figs (10-12) for compounds 3a, 5a and 4 respectively indicate that there is a difference between electrochemical behavior of compounds 3a and 5a than that of compound (4). This result may be explained by the difference in their structure. Table 2 indicates that the potential peaks E_{pa1}, E_{pc1}, E_{pc2}, and E_{pc4} have nearly the same values; this result may be argued to the presence of Ph-N=C group in the three investigated compounds.

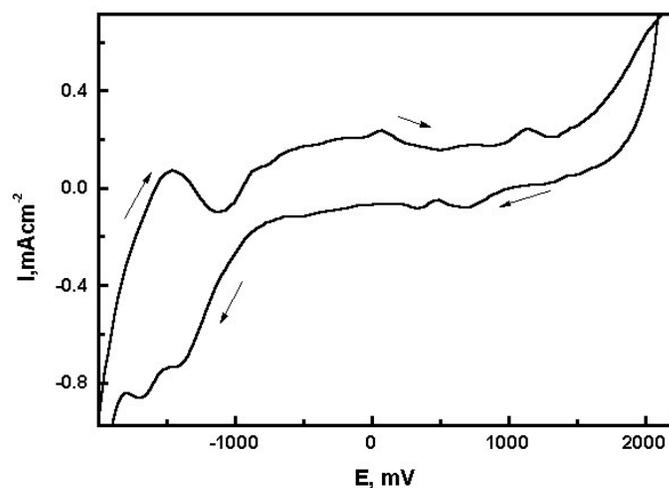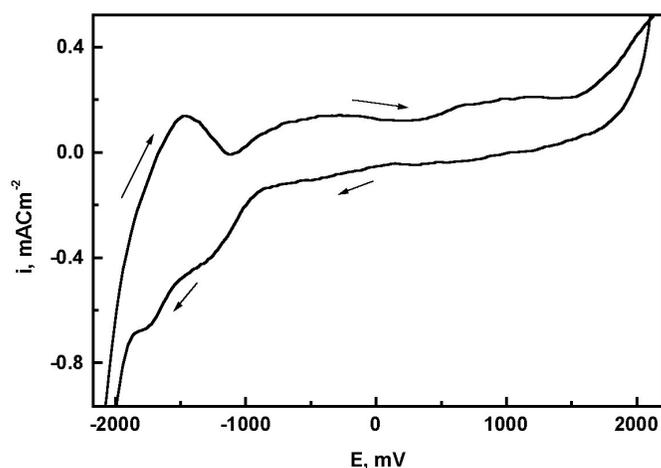**Figure 10.** The cyclic voltammogram of compound (3a) in a solution of 0.1 M (Et)$_4$NClO$_4$ / acetonitril at scan rate 500 mVs^{-1} .

Figure 11. The cyclic voltammogram of compound (5a) in a solution of 0.1 M (Et)$_4$NClO$_4$ / acetonitril at scan rate 500 mVs^{-1}.
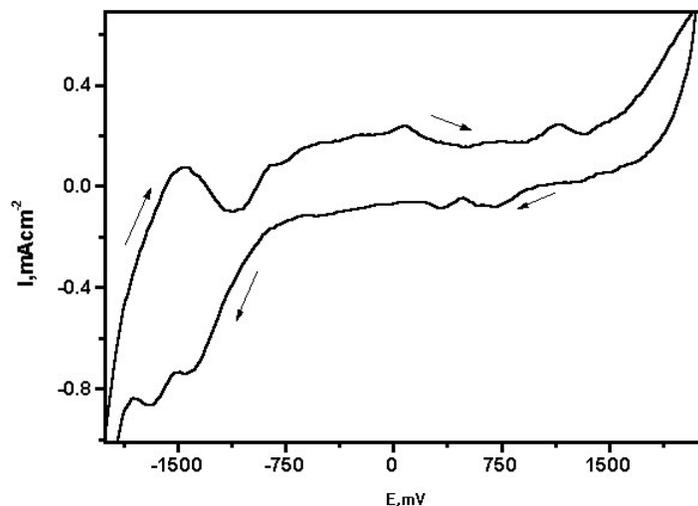
Figure 12. The cyclic voltammogram of compound (4) in a solution of 0.1 M (Et)₄NClO₄ / acetonitril at scan rate 500 mVs^{-1}.

The appearance of a new peak in the cyclic voltammogram of compounds 3a, 4,and 5a around –1450 mV nearly comparing with the cyclic voltammogram of compound 2a in fig (2), this results may be argued to the release of one hydrogen proton from Ph-NH group in compound (2a). The presence of anodic potential peaks at –75 mV and –432 mV in the cyclic voltammogram for each compound 3a and 4 respectively, and disappear of these peaks in cyclic voltammogram of compound (5a) .This result can be attributed to the presence of cyano group in both compound 3a and 4, where cyano group have a high electron withdrawing ability [50]. The E_{pc} values of compound (4) are more negative compared to that of the parent compound (2a), this result can be argued to increasing a proton acceptor in compound (4) [51]. The compounds (5a-5e) are the oxidized form of compounds (2a-2e) by losing two hydrogen protons during its reaction with TCNE. We get the same compounds by the electrooxidation of substituted thiosemicarbazones (2a-2g), i.e. thiadiazoles can be obtained by the electrochemical oxidation and the chemical oxidation. Tables 1 and 2 indicate that the reversibility of product compounds is higher than the starting compounds (2a-2e); this indicates that the products are more stable under the experimental conditions [51]. The stability of the products 3a, 4, 5a is in the following order 5a > 3a > 4, this can be indicated by the difference in the heights of anodic peak current [52]. Despite of effect of side chain on the electrochemical behavior of other substitutions for thiosemicarbazone may be undergoing for further work.

Table 2. The redox potentials of compounds 3a, 4, and 5a vs. SCE

compound	E_{pa1}	E_{pa2}	E_{pa3}	E_{pc1}	E_{pc2}	E_{pc3}	E_{pc4}	E_{pc5}
3a	-1485	-75	1155	-1691	-1420	339	702	1257
4	-1463	-432	935	-1754	-1307	-500	810	----
5a	-1450	80	1150	-1680	-1439	339	705	----

References

1. K.Janardhan Reddy, J.Rajesh Kumar, C. Ramachandraiah, T. Thriveni, A. Varada Reddy. *Food chemistry* 101 (2007) 0585
2. D.X.West, S.B. Padhye, P.B. Sonawane, *Struct.Bond.*76 (1991) 76.
3. F.A.Freench, E.J.Blanz, Jr., S.C. Shaddix, R.W.Brockman, *J. Med. Chem.*17 (1974)172.
4. F.A.Freench, E.J.Blanz, Jr., *Cancer Res.*26 (1996) 1638.
5. W. Antholine, J. Knight, H. Whelan, D.H. Petering, *Pharm.*13 (1977) 89.
6. D. Kovala-Demertzi, M. A. Demertzis, J. R. Miller, C. Padadopoulou, C. Dodorou, G. Filousis, *J. Inorg. Biochem.* 86 (2001) 555.
7. A. G, Quiroga, J. M. Perez, L. Solera, J. R. Masaguer, A. Luque, P. Román, A. Edwards, C. Alonso, C. N-. Ranninger, *J. Med. Chem.* 41 (1998) 1399.
8. D. H. Petering, *Bioinorg. Chem.* 1 (1972) 255.
9. D. Kovala-Demertzi, A.Domopoulou, M.A. Demertzis, G. Valle, A.Papageogiou, *J. Inorg. Biochem.*68 (1997) 147.
10. D. Kovala-Demertzi,P. N. Yadav, M. A. Demertzis, M. Coluccia, *J. Inorg. Biochem.* 78 (2000) 347.
11. Singh, R. B., Gang, B. S., and Singh, R. P., Analitical applications of thiosemicarbazones: A review. *Talanta* 25 (1978) 619.
12. A. Billabert, M. Callaquin and M. Hamon, *Analusis* 3 (5), (1975) 258.
13. A. Billabert and M. Hamon, *Analusis* 5 (1), (1977) 29
14. H. Hoffmann, G. Loeber and W. Schulze, *Stud. Biophs.* 117 (1987) 9.
15. Carolina Ringol, C. Olea-Azar, Fernando Mendizábal, Lucia Otero, Dinorah Gambino, Mercedes Gonzábal, *Huge Cerecetto spectrochemica Acta Part A* 61 (2005) 2933.
16. Jingwan Kang, Zhifeng Li, Xiaoquan Lu, Yongsheng Wang , *Electrochemica Acta* 50 (2004) 19.
17. R. M. El-Shazly, G. A. A. Al-Hazmi, S. E. Ghazy, M. S. El-Shahawi, A. El-Azmy, *Spectrochemica Acta Part A* 61 (2005) 243.
18. Rajeev C. Chikate, Avadhoot R. Belapure, Subhash B. Padhye, Dauglas X. West. *Polyhedron* 24 (2005) 889
19. G. A. A. Al-Hazmi, M. S. El-Shahawi, I. M. Gabr and A. A. El-Asmy, *J. of Coordination chemistry*. 58(8) (2005) 713
20. G. A. A. Al-Hazmi, M. S. El-Shahawi, A. A. Al-Asmy, *Transition Metal Chemistry*, 30 (2005) 464
21. Dipankar Mishra, Subhendu Naskar, Michael G.B. Drew, Shyamal Kumar Chattopadhyay. *Inorganic Chemica Acta* 359 (2006) 585
22. R. P. John, A. Streekanth, V. Rajakannan, T. A. Ajith, M. R. P. Kurup, *Polyhedron* 23 (2004) 2549.
23. A. Arquero, M. A. Mendiola. P. Souza, M. T. Sevilla, *Polyhedron* 15 (1996) 165.
24. Z. Durackova, M. A. Mendiola, M. T. Sevilla, A. Valent, *Bioelectrochem. Bioenerg.* 48 (1999) 109.
25. A. A. El-Asmy, Y. M. Shaibi, I.M. Shedaiwa, M. A. Khattab, *Synth. Rect. Inorg. Met. Org. Chem.*20 (1990) 461.
26. X. Du, E. Hansell, J.C. Engel, C.R. Carey, F.E. Cohen, J.H. Mc Kerrow, *Chem.Biol.*7 (2000) 733.
27. X. Du, C. Guo, E. Hansell, P.S. Doyle, C.R. Carey, T.P. Holler, J.H.McKerrow, F.E.Cohen, *J. Med. Chem. 45* (2002) 2695.
28. H.A.O. Hill, D.J. Page, N. J. Walton and D. Whitford, J. Electroanal. Chem., 187 (1985) 315.
29. H.A.O. Hill, D.J. Page, N. J. Walton and D. Whitford, J. Electroanal Chem., 217 (1987) 129.
30. H.A.O. Hill, D.J. Page, N. J. Walton and D. Whitford, *J. Electroanal Chem.*, 208 (1986) 395.
31. R. Beckert, M. G. Gruner, I. Seidel, R. Kuban, Monatsh. Chemie. 120 (1989).1125 .
32. P. Carloni, L. Greci, P. Stipa, D. Dopp, A. Hassan, A.Alberti.*Tetrahedron*, 51 (1995) 7451.
33. G. Farsang, M. Kovacs, T.M. H.Saber and L. Ladanyi. *J. Electroanal. Chem.*, 38 (1972).

34. J. T. Wang, Y. W. Zhang, Y. M. Xu, Z. W. Wang, *Heteroatom Chemistry*, 6 (1995) 443.

35. L. S. Pinheiro and M. L. A. Temperini *J. Electroanal. Chem.,* 295 (1990) 169.

36. A. A. Hassan, N. K. Mohamad, A. M. Shawky, D. Döpp, *Arkivoc*. 2003(i), (2003) 118.

37. Mohsen A. -M. Gomaa, Alaa A. Hassan, and Hamdy S. Shehatta, *Heteroatom Chemistry* 17, 4 (2006) 261

38. G. M. Abdou-Elenien. N. A. Ismail. M. M. Hassanin and A. A. Fahmy. *Can. J. Chem.*, 70 (1992) 2704.

39. G. S. Patterson. R. H. Holm. *J. Bioinorg. Chem.* 4 (1975) 1257.

40. R. J. Waltman, A. F. Diaz, and J. Bargon, *J. Phys. Chem.,* 87 (1983) 1459; G. Tourillon and F. Garnier, *ibid. 87 (1983) 2289.*

41. G. Horn and W.Schulze, *Bioelectrochemistry and bioenergetics*, 27 (1991) 221.

42. A. J. Brad, L. R. aulkner, "*Electrochemical Methods fundamental and   Applications* ", John Wiley, New York, 1980, p.218.

43. G. Farsang, M. Kovacs, T. M. H. Saber and L. Ladanyi*, J. Electroanal. Chem.* 74 (1976) 205.

44. M. E. Peover and B. S. White, *J. Electroanal. Chem.*, 13 (1967) 93

45. S. Damiele, P. Ugo and G. A. Mazzochin, *J. Electroanal. Chem.*, 267 (1989) 129.

46. J. M. Saveant and E. Vianello, *Electrochim.Acta*, 8 (1963) 905.

47. R. N. Nicholson and I. Shain , *Anal. Chem.*, 36 (1964) 706

48. A. J. Fataidi, *Synthesis*, 249 (1986).

49. F.Gerson; G.Geschaidt; R.Mockel, A.Aumuller; P.Erk; S.Hunig, Helv.*Chim.Acta*, 71 (1988) 1665.

50. P. Carloni, L. Greci, P. Stipa, D. Döpp,A. A. Hassan, A. Alberti, *Tetrahedron*, 51(27), (1995) 7452

51. G. Farsang, M. Kovacs, T. M. H. Saber and. Ladanyi. *J. Electroanal. Chem.*, 38(1972)127

52. J. Luduik, J. Volke and J. Klima. *Electrochemica Acta.* 32(7), (1987) 1063