Journal of the Korean Chemical Society
2006, *Vol. 50, No. 4*
Printed in the Republic of Korea

몇 가지 치환 Thiadiazole에 대한 전기화학적 연구

A. A. El Maghraby*, G. M. Abou-Elenien, N. A. Abdel-Reheem, and H. R. Abdel-Tawab
Chemistry department, Faculty of science, Cairo University, Giza, Egypt
(2006. 3. 20 접수)

Electrochemical Studies on Some Substituted Thiadiazoles

A. A. El Maghraby*, G. M. Abou-Elenien, N. A. Abdel-Reheem, and H. R. Abdel-Tawab
Chemistry department, Faculty of science, Cairo University, Giza, Egypt
(Received March 20, 2006)

요 약. 2-Ketohydrazono-3-phenyl-5-substituted-2,3-dihydro-1,3,4-thiadiazole과 그 유도체들(**1a-h**)의 산화환원 특성을 백금 전극의 지지전해질로서 0.1 M tetra n-butylammonium perchlorate (TBAP)을 함유한 1,2-dichloroethane (DCE), dichloromethane (DCM), acetonitrile (AN), tetrahydrofuran (THF), and dimethylsulfoxide (DMSO)와 같은 비수용매 속에서 조사하였다. 조사한 화합물들의 산화 및 환원 생성물들을 조절전위 전해법으로 분리 확인하였으며, 산화환원 메커니즘을 제안하고 이를 증명하였다. 조사한 모든 화합물은 잘 알려진 EC 메커니즘에 이은 두 번의 비가역 일전자 과정에 의해 산화되는 반면, 환원의 경우에는 치환기의 성질에 따라, 잘 알려진 EEC 메커니즘에 이은 한번의 이전자 또는 두 번의 연속적인 일전자 과정에 의해 이루어짐을 알았다.

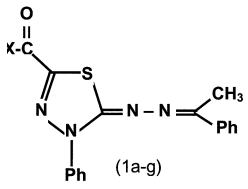
주제어: 치환 Thiadiazole 유도체, 산화환원 생성물, 산화환원 메커니즘

ABSTRACT. The redox characteristics of 2-ketohydrazono-3-phenyl-5-substituted-2,3-dihydro-1,3,4-thiadiazoles and its derivatives (1a-h) has been investigated in nonaqueous solvents such as 1,2-dichloroethane (DCE), dichloromethane (DCM), acetonitrile (AN), tetrahydrofuran (THF), and dimethylsulfoxide (DMSO) containing 0.1 mol.dm^{-3} tetra –n-butylammonium perchlorate (TBAP) as supporting electrolyte at platinum ectrode. Through controlled potential electrolysis, the oxidation and reduction products of the investigated compounds can be separated and indentified. The redox mechanism is suggested and proved. It was found that all the investigated compounds are oxidized in two irreversible one-electron processes following the well known pattern of EC-mechanism. On the other hand, these compounds are reduced in a single two electron or in a successive two one electron processes following the well known pattern of EEC-mechanism according to the nature of the substituent

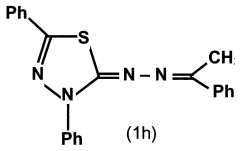
Keywords: Substituted Thiadiazoles, Oxidation and Reduction Products, EC-Mechanism

INTRODUCTION

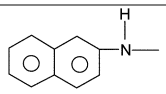
Thiadiazoles and its derivatives are known to have many biological applications. Recently some thiadiazoles, already being included in several compounds that have potential use in treatment of diseases, as anti-inflammatory agent[1], anti-influenza agent[2] and anti-protozoal durg[3]. They deserve consideration, as a fertilizer amendment for retarding nitrification fertilizer N in soil[4] and induce acquired resistance in wheat[5]. An important potential use in the removal of cadmium from waste water and other portable waters[6]. Because of this and continuing interest of our laboratory in the electrochemistry of the biologically active organic compounds[7-14]. It was found worthwhile to investigate the redox



(1a-g)



(1h)

Compounds	Series I X
1a	Ph—N(H)—
1b	H_3C —
1c	Ph —
1d	Et —O—
1e	
1f	
1g	

characteristics of substituted thiadiazoles (1a-h). These compounds were extensively studied using cyclic voltammetry in nonaqueous solvents. The number of electrons participating in each electrode reaction was determined using the coulometeric technique. Separation and identification of the intermediates and the final products were made through the controlled potential electrolysis (CPE).

EXPERIMENTAL

The organic compounds are synthesized according to the procedures outline in literature[15]. All the synthesis compounds were purified by repeated crystallization, dried under reduced pressure and the purity was checked by thin layer chromatography.

The measurements were carried out using the following apparatus: The EG& G Princetion applied research model 283 Potentiostat / Galvanostat controlled from a PS-486-DX microcomputer via a National Instrument IEEE -488 through GPIB board by means of M270/250 program was used for the electrochemical control.

All measurements were carried out with 2.5×10^{-5} mol of the reactant in 15 ml dry oxygen free solvent with 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate as supporting electrolyte. 1,2-dichloroethane (DCE), Dichloromethane (DCM), acetonitrile (AN), tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) were used as solvents.

During the solvent purification, all the processes were performed under a dry oxygen-free argon atmosphere. Fractionation was carried out using a 120 cm column filled with glass spirals at a recoil ratio of 50 : 1. All purified solvents were stored under argon in the dark. Purification of the different solvents was carried out as follows: $EtCl_2$ (Merck, P.a.) was boiled for 24 h with PCl_5 and then distilled. The main fraction was stirred with $KMnO_4$ for 24 h and distilled, finally, the solvent was fractionated.

AN was purified according to the modified methods of Walter and Rumaloy[16-17].

THF (Uvasol Merck) was boiled successively for 12 h with calcium hydride (Merck), 12 h with basic aluminium oxide (Woelm, Act. I), 6 h with sodium metal and 6 h with potassium metal and distilled after each process. In the last two steps the solvent was fractionated.

DMSO (Merck) was boiled four times with calcium hydride (Merck) for 14 h (5 g/L) and subsequently fractionated at 14 Torr. Finally, the main fraction was carefully fractionated.

The working electrode was a Pt electrode 1.3 mm in diameter, the auxiliary electrode was Pt wire immersed in the corresponding electrolyte. The reference electrode was Ag /AgCl / Cl^- (sat. AN) and the redox potential ($E_{1/2}$) values are referred to the potential of cobaltocinuim/cobaltocene system[18].

Controlled Potential Electrolysis (CPE)

CPE experiments were carried out in dry acetonitrile containing 0.1 mol. dm^{-3} tetra-n-butylammonium perchlorate (TBAP) as supporting electrolyte, compound 1b is reported here as example. The potential was controlled at the current plateau of the

oxidation or reduction peaks (300 mV more positive or more negative than the E_p in oxidation and reduction processes, respectively). As a working electrode, a platinum gauze electrode (ca. 80 cm^2) was used. The progress of the electrolysis was followed by recording periodically the decrease in current with time. From time to time the working electrode was removed from the cell, sprayed with pure acetone and burned in a direct flame, cooled and replaced in the cell. After the electrolysis was completed, the cell was disconnected from the circuit and the solvent was evaporated in vacuum. The residue was shaken with dry ether and the supporting electrolyte was filtered off. The ethereal layer was evaporated in turn. The obtained residue was chromatographed on thin layer silica gel plates using chloroform as an eluent. The main electrolysis product obtained was scraped off the plate and extracted with acetonitrile, filtered and evaporated in vacuum. The resulting solid compound was identified.

Oxidation product of 1c

Oxidation of 1c to give: Methyl-[5-(1-phenyl-ethylidene)-5H-3-thia-1,4,5,9b-tetraazacyclopenta[a] naphthalen-2-yl]-methanone(m.p.: 165°C, yield 67%).

Analytically calculated: C, 69.52%; H, 4.28%; N, 14.10%; S, 8.06%.

Found: C, 69.31%; H, 4.22%; N, 13.97%; S, 8.00%.

^{1}H NMR ($CDCl_3$, TMS): 2.50 (s, 3H, CH_3); 7.26-7.89 (m, 14H, Ar H's);

Mass spectrum: Shows the main fragments at m/z 397, parent; 293 [M^- - ($CH-(CH_3)_2$)]; 203 (M^- - N_2); 101 (M^- - [-C – N – C_6H_4)].

Cxidation product of 1a

Reduction of 1b to give: Bis (5E)-2-(anilinocarbonyl)-5-(1-phenyleythylidene)-5H-[1,3,4]-thiadiazolo[2,3-c][1,2,4]benzotriazin-5-ium] (m.p.: 269°C, yield 55%).

Analytically calculated: C, 67.15%; H, 4.14%; N, 17.03%; S, 7.79%.

Found: C, 67.21%; H, 4.05%; N, 16.97%; S, 7.68%.

IR spectrum (KBr) is characterized by the disappearance of the band 3364 cm^{-1} (NH) in comparison with that obtained for the original compound 1a.

^{1}H NMR ($CDCL_3$, TMS) and also D_2O exchange with that obtained with the oxidation product showed that nh-band (8.1) disappeared through the oxidation process

Mass spectrum: Shows the main fragments at m/z 822 parent; 411 (M^-/2), 307(M^-/2–[–C ($CH_3)_2$)]; 279 (M^- – (N_2)); 177 (M^- – (–C–N– C_6H_5)).

Reduction product of 1c

Oxidation of 1c to give: (1E)-1-phenylethanone [(2E)-5-[hydroxyl(phenyl) methyl]-3-phenyl-1,3,4-thiadiazol-2(3H)-ylidene] hydrazone (m.p.: 162°C, yield 67%).

Analytically calculated: C, 68.98%; H, 5.03%; N, 13.99%; S, 8.01%.

Found: C, 68.87%; H, 4.00%; N, 13.88%; S, 7.94%.

^{1}H NMR ($CDCl_3$, TMS): 2.50 (s, 3H, CH_3); 5.83 (s, 1H, CH), 7.22-7.93 (m, 15H, Ar H's); 11.21 (s, br, 1H, OH).

Mass spectrum: Shows the main fragments at m/z 400

Reduction product of 1a

Reduction of 1b to give: (1E)-1-(aniline)ethanone [(2E)-5-[hydroxyl(phenyl) methyl]-3-phenyl-1,3,4-thiadiazol-2(3H)-ylidene] hydrazone (m.p.: 210°C, yield 57%).

Analytically calculated: C, 66.48%; H, 5.09%; N, 16.85%; S, 7.72%.

Found: C, 66.43%; H, 5.05%; N, 16.78%; S, 7.68%.

IR spectrum (KBr) is characterized by the disappearance of the band 1685 cm^{-1} (C =O) in comparison with that obtained for the original compound 1a.

^{1}H NMR ($CDCL_3$, TMS): 2.50 (s, 3H, CH_3); 5.83 (s, 1H, CH), 7.22-7.93 (m, 15H, Ar H's); 11.21 (s, br, 1H, OH), s, 1H, NH)

Mass spectrum: Shows the main fragments at m/z 415 parent;, 307(M^-/2–[–C ($CH_3)_2$)]; 279 (M^- – (N_2)); 177 (M^- – (–C–N– C_6H_5)).

RESULTS AND DISCUSSION

Cyclic voltammetric data are listed in *Table* 1. *Fig.* 1 show as an example the cyclic voltammogram of some investigated compounds. Compounds (1a-h) are oxidized in two irreversible one-electron process following the well known pattern

Table 1. C. V. data of compounds (1a-h) at pt-electrode in different solvents (Scan rate = 100 mV/s)

Compounds	Sol.	D.N.	Temp.	Reduction		Oxidation		ΔE = EpO - EpR	Log K
				EpI (V)	EpII (V)	EpI (V)	EpII (V)		
	DCM	1.000	0°C	- 2.089	-	1.285	1.482	3.374	57.186
	DCE	0.100	25°C	- 1.918	-	1.324	1.594	3.242	54.949
1a *	AN	14.100	25°C	- 1.804	-	1.244	1.564	3.048	51.661
	THF	20.000	0°C	- 1.590	-	1.427	-	3.017	51.135
	DMSO	29.800	25°C	- 1.780	-	1.220	-	3.000	50.847
	DCM	1.000	0°C	- 1.689	-	1.351	1.527	3.040	51.525
	DCE	0.100	25°C	- 1.716	-	1.297	1.513	3.013	51.067
1b	AN	14.100	25°C	- 1.566	-	1.275	1.571	2.841	48.152
	THF	20.000	0°C	- 1.836	-	1.527	-	3.363	57.000
	DMSO	29.800	25°C	- 1.515	-	1.248	-	2.763	46.830
	DCM	1.000	0°C	- 1.445	- 1.864	1.324	1.513	2.769	46.930
	DCE	0.100	25°C	- 1.459	- 1.878	1.297	1.648	2.756	46.710
1c	AN	14.100	25°C	- 1.322	- 1.891	1.270	1.598	2.592	43.932
	THF	20.000	0°C	- 1.594	-	1.432	-	3.026	51.288
	DMSO	29.800	25°C	- 1.284	-	1.248	-	2.532	42.915
	DCM	1.000	0°C	- 2.000	-	1.345	1.545	3.345	56.690
	DCE	0.100	25°C	- 2.000	-	1.318	1.484	3.318	56.237
1d	AN	14.100	25°C	- 1.802	-	1.270	1.582	3.072	52.067
	THF	20.000	0°C	- 1.770	-	1.459	-	3.279	54.732
	DMSO	29.800	25°C	- 1.745	-	1.236	-	2.981	50.525
	DCM	1.000	0°C	- 1.432	- 1.851	1.337	1.500	2.769	46.932
	DCE	0.100	25°C	- 1.445	- 1.878	1.310	1.510	2.755	46.694
1 e	AN	14.100	25°C	- 1.303	- 1.837	1.273	1.593	2.576	43.661
	THF	20.000	0°C	- 1.700	-	1.418	-	3.118	52.845
	DMSO	29.800	25°C	- 1.240	-	1.250	-	2.490	42.203
	DCM	1.000	0°C	- 1.454	- 2.090	1.345	1.563	2.799	47.440
	DCE	0.100	25°C	- 1.450	- 2.060	1.303	1.540	2.753	46.660
1f**	AN	14.100	25°C	- 1.272	- 1.810	1.280	1.552	2.562	43.254
	THF	20.000	0°C	- 1.810	-	1.432	-	3.242	54.962
	DMSO	29.800	25°C	- 1.212	-	1.260	-	2.472	41.898
	DCM	1.000	0°C	- 1.418	- 2.127	1.400	1.581	2.818	47.762
	DCE	0.100	25°C	- 1.403	- 2.140	1.350	1.543	2.753	46.661
1g	AN	14.100	25°C	- 1.285	- 2.165	1.295	1.575	2.580	43.728
	THF	20.000	0°C	- 1.620	-	1.480	-	3.100	52.541
	DMSO	29.800	25°C	- 1.200	-	1.264	-	2.464	41.762
	DCM	1.000	0°C	-	-	1.149	1.462	-	-
	DCE	0.100	25°C	-	-	1.029	1.514	-	-
1h	AN	14.100	25°C	-	-	1.129	1.473	-	-
	THF	20.000	0°C	-	-	1.200	-	-	-
	DMSO	29.800	25°C	-	-	1.145	-	-	-

*There is another peak in AN at E_p = 2.036 (V), in DCE at E_p = 1.864 (V), in DCM at E_p = 1.892 (V).
**There is another peak in AN at E_p = 2.072 (V), in DCE at E_p = 1.900 (V), in DCM at E_p = 1.963 (V).

of EC-mechanism. The first electron will follow by a proton removal from the ortho-position in the N-phenyl ring forming the radical then followed by the second electron uptake from the second nitrogen atom in the N=C group forming the unstable intermediate (di-radical cation) which undergoes a ring closure forming the corresponding cation. The formed cation can be stabilized in solution through

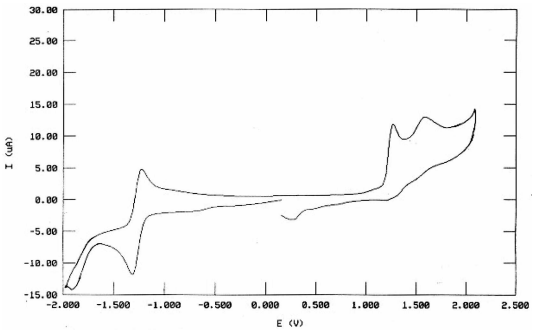


Fig. 1. CV-voltammogram of compound 1c in AN at Pt-electrode (scan rate = 100 mV/s; T = 25 °C).

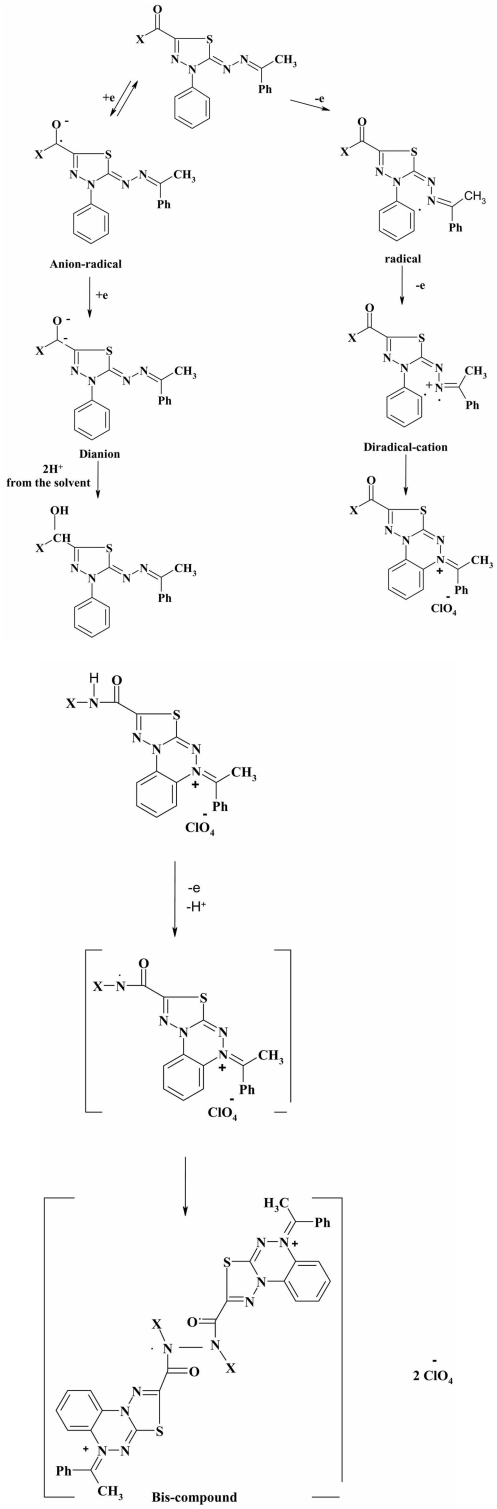
its combination with a perchlorate anion from the medium. Compounds which contain NH group (1a, 1f) undergo further oxidation. The NH will be oxidized through electron uptake followed by proton–removal to give the corresponding radical, which undergoes a dimerization reaction to give the bis compound (*Scheme* 1). On the other hand the reduction center in the investigated compounds seems to be the carbonyl group (C=O). The absence of this group in compound 1h is the reason for the disappearance of reduction peaks. In quasi-reversible one electron processes, these compounds are reduced to give the more or less stable anion-radical. The stability of this anion-radical can be seen from the shape of the reduction peak and also from the values of ΔE_p and I_p^c/I_p^a. The increase of the withdrawing power of the substituent, make possible for a second electron reduction wave to give the dianion, which is basic enough to abstract protons from the media to saturate the (C=O) bond (*Scheme* 1).

3.1. Substituent Effect

The effect of substituents on both oxidation and reduction of an electroactive site can be illustrated by applying the well-known modified Hammett equation of the form[19].

$$E_p^* = \rho_x \sigma_x + E_p^H \qquad (1)$$

Where σ_x is the Hammett constant, ρ_x is the polarographic reduction or oxidation constant and E_p^*, E_p^H are the peak potential of the substitued and



Scheme 1.

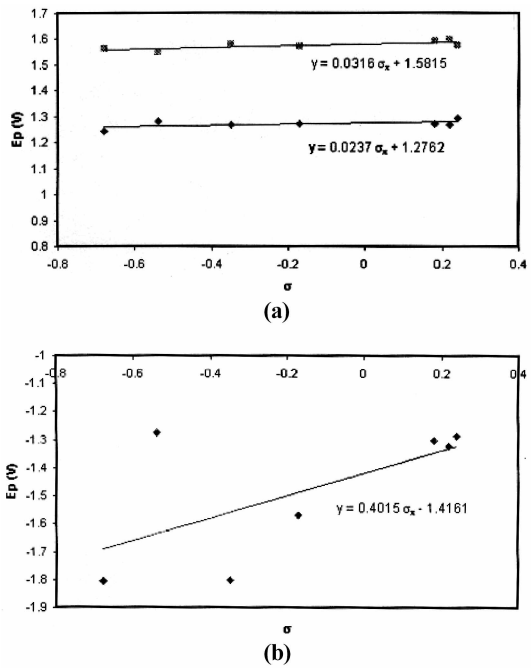


Fig. 2. Dependence of E_p (ox) of compound (1a-h) in AN on Hammett substitution constant (σ).

Table 2. The Hammett equations of the regression lines obtained for the series (1a-h)

Solvent	Equation of series 1a -h
AN	$(E_p^{ox})_I = 0.0237\,\sigma_x + 1.2762$ (Oxidation)$_I$
	$(E_p^{ox})_{II} = 0.0316\,\sigma_x + 1.5815$ (Oxidation)$_{II}$
	$(E_p^{red}) = 0.4015\,\sigma_x - 1.4161$ (Reduction)
DCE	$(E_p^{ox})_I = 0.0057\,\sigma_x + 1.3150$ (Oxidation)$_I$
	$(E_p^{ox})_{II} = 0.0169\,\sigma_x + 1.5501$ (Oxidation)$_{II}$
	$(E_p^{red}) = 0.4261\,\sigma_x - 1.5603$ (Reduction)
DCM	$(E_p^{ox})_I = 0.0488\,\sigma_x + 1.3487$ (Oxidation)$_I$
	$(E_p^{ox})_{II} = 0.0153\,\sigma_x + 1.5325$ (Oxidation)$_{II}$
	$(E_p^{red}) = 0.5344\,\sigma_x - 1.5627$ (Reduction)
THF	$(E_p^{ox}) = 0.0121\,\sigma_x + 1.4555$ (Oxidation)
	$(E_p^{red}) = 0.0822\,\sigma_x - 1.6899$ (Reduction)
DMSO	$(E_p^{ox}) = 0.0223\,\sigma_x + 1.2501$ (Oxidation)
	$(E_p^{red}) = 0.4269\,\sigma_x - 1.3581$ (Reduction)

unsubstituted compounds respectively. *Fig.* 2a, b illustrate the Hammett equation correlations of the peak potentials of compounds (1a-h) for both oxidation and reduction processes. The equations of the regression lines obtained for the series (1a-h) are listed in *Table* 2.

It is obvious from equations in *Table* 2 that the magnitude of the oxidation constant ρ_x^{ox} is smaller than that of the corresponding reduction constant ρ_x^{red}. This indicates that the electroreduction is much more susceptible to substituent effect than electroxidation. This fact implies that, there is more significant resonance interaction between the substituent and the reduction center (C=O group) which is in good agreement with proposed reduction of adjacent C−O group, while the oxidation center (N−C group) is far away from the substituents.

To show the effect of solvent on the redox mode of the investigated compounds, the electrochemical characteristics of these compounds are extensively studied in 1,2-dichloroethane (DCE), dichloromethane (DCM), acetonitrile (AN), tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) with 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate as supporting electrolyte. The voltammetric data are listed in *Table* 1. As shown from the data and voltammograms (*Fig.* 1) compounds (1a-h) show that both oxidation and reduction of all the investigated compounds proceed identically in DCE, DCM and AN, they are oxidized in two irreversible one-electron transfer to the diradical cation which in turn undergoes a follow up chemical reaction with ring closure; and reduced in one or two-electron processes to the stable anion radical or to the full saturation of the (C=O) group according to the nature of the substituent (*Scheme* 1). The requirements for reversibility in the reduction process are satisfied, at least at low scan rates, in the three solvents for those compounds which undergo a reversible or quasi-reversible reduction. In THF and DMSO (*Fig.* 3) the oxidation and also the reduction proceed in one two electron wave. The radical or the anion – radical formed during the first electron lost or gained are unstable , therefore the second electron transfer followed immediately. Going from DCE to DMSO (increasing the donor number from 0.1 to 29.8)[20], makes both the oxidation and reduction of these thiadiazoles easier. This behavior can be attributed to a solvation effect, as already reported by many workers[20-22]. *Fig.* 4, represents the relationship between ΔE_p of compound 1d and the donor number of the solvents

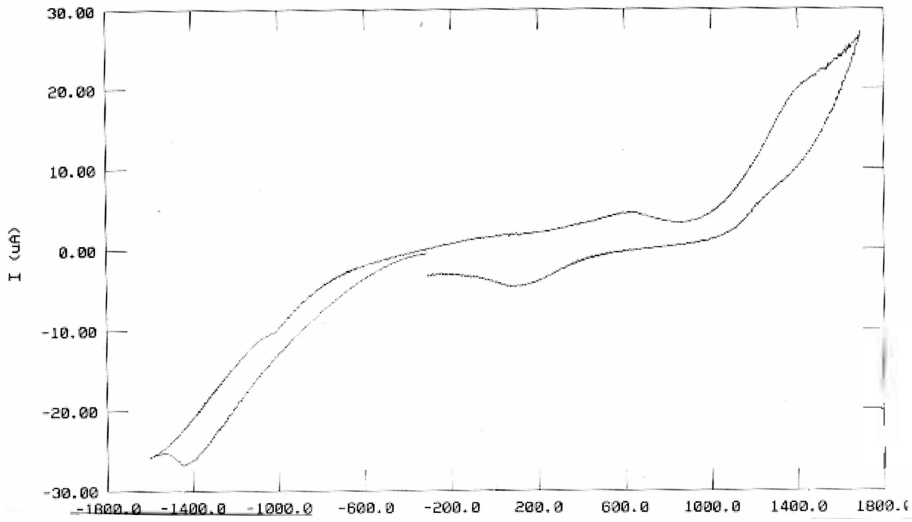


Fig. 3. CV-voltammogram of compound 1a in THF at Pt-electrode (scan rate = 100 mV/s; T = 25 °C).

According to the Born-Haber cycle[23] the E_p values for one thiadiazole in two different solvents A and B and the salvation energies of the corresponding ions can be derived as follows

$$
\begin{aligned}
&F(\Delta E_p^{ox} - \Delta E_p^{red}) \\
&= F\{[E_p^{ox}(A) - E_p^{ox}(B)] - [E_p^{red}(A) - E_p^{red}(B)]\} \\
&= F\{[E_p^{ox}(A) - E_p^{red}(A)] - [E_p^{ox}(B) - E_p^{red}(B)]\} \\
&= -\delta\Delta G_{solv}(TD^+, A) + \delta\Delta G_{solv}(TD^+, B) \\
&\quad - \delta\Delta G_{solv}(TD^-, A) + \delta\Delta G_{solv}(TD^-, B) \\
&= [\delta\Delta G_{solv}(TD^+, B) + \delta\Delta G_{solv}(TD^+, B)] \\
&\quad - [\delta\Delta G_{solv}(TD^-, A) - \delta\Delta G_{solv}(TD^-, A)]
\end{aligned}
$$

where TD represents the thiadiazole derivative, $\delta\Delta G_{solv}$ is the differential Gibbs solvation energy, F, is the faraday constant and $E_p^{ox} - E_p^{red} = \Delta E_p$ is the difference between the oxidation and reduction peaks potential in the same solvent. According to the equation, when the solvent is change the sum of the solvation energies is greater if ΔE_p is smaller. As can be seen in *Table* 1; ΔE_p for all the investigated thiadiazoles (1a-h) decreased when the solvent changed from 1,2-dichloroethane to DMSO; i.e. the sum of the solvation energies increased which is full agreement with rhe results obtained for hydrazyl[18-20]. This is in accordance with Gutmann's donor model[20]. In all cases there is a linear relationship between the electrochemical parameters (E_p, ΔE_p and log k) and the donor number (*Fig.* 4). Accordingly, the sum of the solvation energies of a particular thiadiazole in a given solvent depend on the donor number of the solvent. This suggests that solvation process is mainly attributable to electrostatic interaction. It is possible that the unusual results for the oxidation and reduction of all the investigated thiadiazoles in THF is due to perturbation of the solvent by, for example, formation of an ion pair[18,24,25]. On the basis of substituent dependence it is expected that the oxidation potential will decrease, while the reduction potential will increase, when the substituent is less electronegative. Also, the solvation of the formed ion radical of two different substituted thiadiazoles in the same solvent

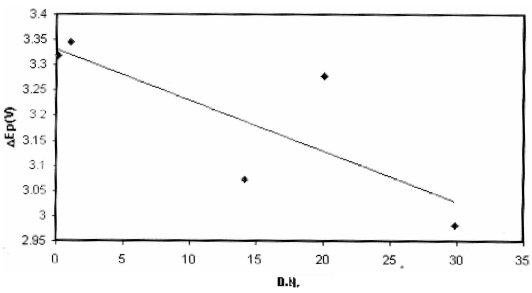


Fig. 4. Dependence of ΔE_p of compound 1d on the donor number of the solvents.

Table 3. Difference in solvation energies of one thiadiazole ion radical in two different solvents at 25 ℃

Solvent transition	$F(\Delta E_p)_A$ - $F(\Delta E^{-}_{p})_A$ in two different solvents						
	1a	1b	1c	1d	1e	1f	1g
DCM → DCE	F(132)	F(027)	F(013)	F(027)	F(014)	F(046)	F(065)
DCE → AN	F(194)	F(172)	F(164)	F(246)	F(179)	F(191)	F(173)
DCM → AN	F(326)	F(199)	F(177)	F(273)	F(193)	F(237)	F(238)

can be expressed as follows according to the principle of the cyclic process[22].

$$F\{[E_p^{ox} - E_p^{red}]_{1b} - [E_p^{ox} - E_p^{red}]_{1c}\} = [\delta\Delta G_{soln}(1b)^{-} + \delta\Delta G_{soln}(1b)^{-} - [\delta\Delta G_{soln}(1c)^{-} + \delta\Delta G_{soln}(1c)^{-}$$

This can only be applied if $I(R) - E_A(R)$ is a constant, where I is the ionization potential and E_A is the electron affinity. *Table* 1 shows a regular increase in ΔE_p for the compounds using different solvents. Taking in consideration the allowed experimental error. The increase follows the order:

$$(\Delta E_p) \approx (\Delta E_p)_{1a} > (\Delta E_p)_{1b} > (\Delta E_p)_{1c} \approx (\Delta E_p) \approx (\Delta E_p) \approx (\Delta E_p)_{1g}$$

i.e. the sum of the solvation energies for compounds in series (1a-h) increase in the order: ic ≈ 1e 1g ≈ 1f > 1b > 1a ≈ 1d

This can be explained from the fact that the substitutents are far away from the oxidation center of the molecules and they only affect the reduction process, which is in full agreements with the proposed mechanism. Accordingly, if it is assumed that the difference in the ionization potentials are small, the change of the solvation energies of the different investigated compounds in different solvents which obtained listed in *Table* 3.

REFERENCES

1. D. G. Ropertson, G. Loewen, K. M. Walsh, L. A. Dethloff, R. S. Sigler, M. A. Dominick and E. R. Urda; *Fundam Appl. Toxicol.* **1993**, *20*, 446.
2. J. M. Collaino, G. M. Birch and J. C. Tang; *Antiviral Chem. Chlemother.*, **1993**, *4*, 271.
3. J. Karoflak-wojciechowska, A. Mrozek, Amiel, Pascale, Brouant, Pierre and J. Barbe,Acta crystallographica, Section C Crystal structure Communincations, **1996**, *52*, 2939.
4. G. W. McCarty and M. J. Bremner, *Soil Sci. Soc. Am.* J., **1990**, *54*, 1017.
5. J. Goerlach, S. Volrath, G. Knuaf-Beiter, G. Hengy, V. Beckhove, K.H. Kogel, M. Oestendrop, T. Staub and J. Ryals, et al. *Plant Cell.*, **1996**, *8*, 629.
6. M. J. Hudson, M. B. Hassan, G. Tiravanti, Hydrometallurgy, **1990**, *24*, 249.
7. G. M. Abou-Elenien, N. A. Ismail, T. S. Hafez, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 651.
8. G. M. Abou-Elenien, M. A. Aboutable, A. O. Sherin, H. M. Fahmy, *J. Chem. Soc. Perkin Trans II*, **1991**, 377.
9. G. M. Abou-Elenien, N. A. Ismail, A. A. Magd Eldin, *Monatsh. Chem.* **1992**, *123*, 1117.
10. G. M. Abou-Elenien, *J. Electroanal. Chem.* **1993**, *346*, 367.
11. G. M. Abou-Elenien, A. A. El Maghraby, H. R. Abdel-Tawab, Electroanalysis, **2001**, *13*, 587.
12. G. M. Abou-Elenien, A. O. Abdelhamid, N. A. Ismail, A. A. El Maghraby, M. A. I. El-Hamadi., Electrochemistry, **2001**, *69*, 652.
13. G. M. Abou-Elenien, N. A. Ismail, A. A. El Maghraby and G. M. Al Abdallah, Electroanalysis, **2001**, *13*, 1022.
14. G. M. Abou-Elenien, N. A. Ismail, A. A. El Maghraby and M. A. I. El-Hamadi., Electroanalysis, **2002**, *14*, 998.
15. A. O. Abdel Hamid, H. A. Emam, N. A. Abdel-Reheem, *J. Chem. Res.*, (S) 532 (M) 2323 (1998).
16. M. Walter, L. Rumaloy, *Anal. Chem.* **1973**, *45*, 165.
17. G. M. Abou-Elenien, Ph. D. thesis, Freiburg, Germany 1980.
18. G. M. Abou-Elenien, *J. Electroanal. Chem.* **1993**, *345*, 303.
19. H. H. Jaffè, *Chem. Rev.*, **1953**, *53*, 191.
20. V. Gutmann, *Monatsh. Chem.*, **1973**, *104*, 990.
21. I. V. Nelson, R. T. Iwamoto, *Anal. Chem.*, **1961**, *33*, 1795.
22. V. Gutmann and R. Schmid, *Monatsh. Chem.*, **1969**, *100*, 2113.
23. B. Case, N. S. Hush, R. Parsons, *J. Electroanal. Chem.* **1965**, *10*, 360.
24. S. Patai (ed) "The Chemistry of Ether linkage" Interscience, London, Ch 6 (1967).
25. S. Searles Jr. and M. Tamres, "Basicity and Complexing Ability of Ethers" Interscience, London, PP, 295 (1967).