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Voltammetric Studies on Some Thiadiazoles and Their Derivatives

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Abstract : The redox characteristics of 2-arylaldehydehydrazono-3-phenyl-5-substituted-2,3-dihydro-1,3,4-thiadiazoles (1a-h) have been investigated in nonaqueous solvents such as 1,2-dichloroethane (DCE), dichloromethane (DCM), acetonitrile (AN), Tetrahydrofuran (THF), and dimethylsulfoxide (DMSO) at platinum electrode. Through controlled potential electrolysis, the oxidation and reduction products of the investigated compounds had been separated and indentified. The redox mechanism had been suggested and proved. It had been found that all the investigated compounds were oxidized in two irreversible one-electron processes following the well-known pattern of The EC-mechanism; the first electron loss gives the corresponding cation-radical which is followed by proton removal from the ortho-position in the N-phenyl ring forming the radical. The obtained radical undergoes a second electron uptake from the nitrogen in the N = C group forming the unstable intermediate (di-radical cation) which undergoes ring closure forming the corresponding cation. The formed cation was stabilized in solution through its combination with a perchlorate anion from the medium. On the other hand, these compounds are reduced in a single two-electron process or in a successive two one-electron processes following the well known pattern of the EEC-mechanism according to the nature of the substituent; the first one gives the anion-radical followed by a second electron reduction to give the dianion which is basic enough to abstract protons from the media to saturate the (C = O) bond.

Keywords : Thiadiazoles, Cyclic voltammetry , Redox characteristics, Non-aqueous solvents, Controlled potential electrolysis.

1. Introduction

Thiadiazoles and their derivatives are known to have many biological applications. Recently some thiadiazoles, have been included in several compounds that have potential uses in treatment of diseases such as anti-inflammatory agents,[1] anti-influenza agents[2] and anti-protozoal drugs.[3] Among the compounds that deserve consideration are those used as fertilizer amendment for retarding nitrification of fertilizer N in soil[4] that induce acquired resistance in wheat.[5] An important potential use of these compounds is in the removal of cadmium from waste water and other potable waters.[6] Because of this there are continuing interest in our laboratory in the electrochemistry of the biologically active organic compounds,[7-16] it was found worthwhile to investigate the redox 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).

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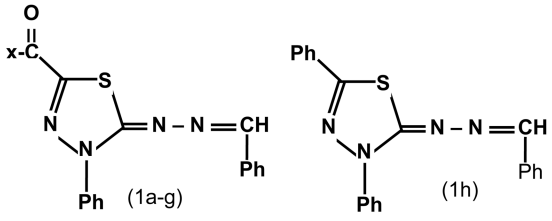
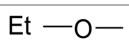
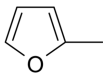
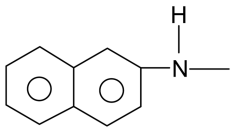
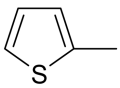
2. Experimental

The organic compounds were synthesized according to the procedure outlined in the literature.[17] All the synthesized compounds were purified by repeated crystal-



Compounds	Series I
	X
1a	
1b	
1c	
1d	
1e	
1f	
1g	

lization, 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 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 [18, 19].

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 potential ($E_{1/2}$) values was referred to the redox potential of cobaltocinuim/cobaltocene system.[18)]

2.1 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 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.

2.1.1 Oxidation product of 1b

Oxidation of 1b to give
:methyl-[5-(1-phenyl-ethylidene)-5H-3-thia-1,4,5,9b-tetraazacyclopenta[a]naphthalen-2-yl]-methanone (m.p.: 152 °C, yield 60%).

Analytically calculated
: C, 63.35%; H, 4.04%; N, 17.39%; S, 9.94%.

Found

: C, 63.24%; H, 3.98%; N, 17.28%; S, 9.83%.

^{1}H NMR ($CDCl_3$, TMS)

:2.60 (s, 3H, CH_3); 7.26-7.79 (m, 9H, Ar H's); 8.4 (s, 1H, CH).

Mass spectrum

: Shows the main fragments at m/z 321, parent; 231 [M^+-(CH-C_6H_5)]; 203 (M^+-(N_2)); 101 (M^+-[-C-N-C_6H_4)].

2.1.2 Reduction product of 1b

Reduction of 1b to give

: (1E)-1-phenylethanone[(2E)-5-(1-hydroxy-ethyl)-3-phenyl-1,3,4-thiadiazole-2(3H)-ylidene] hydrazone (m.p.: 160 ºC, yield 53%).

Analytically calculated

: C, 63.91% ; H, 5.33 %; N, 16.57% ; S, 9.47%.

Found

: C, 63.79%; H, 5.28%; N, 16.39%; S, 9.38%.

IR spectrum (KBr) is characterized by the disappearance of the band 1678 cm^{-1} (C = O) in comparison with that obtained for the original compound 1b.

^{1}H NMR ($CDCL_3$, TMS)

: 2,47 (s, 3 H, CH_3); 2.52 (d, 3 H, CH_3); 7.26-7.98 (m, 10 H , Ar H's); 8.4 (q, IH , CH); 11.1 (s, br., 1H, OH).

Mass spectrum

: Shows the main fragments at m/z 338 parent; 234 (M^+-[-C (CH_3)$_2$)]; 205 (M^+-(N_2)); 103 (M^+-(-C-N- C_6H_5)).

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

Compounds	Sol.	D.N.	Temp.	Reduction		Oxidation		DE = E_pO - E_pR	Log K
				E_{pI} (V)	E_{pII} (V)	E_{pI} (V)	E_{pII} (V)		
1a *	DCM	1.000	0 °C	-2.054	-	1.272	1.690	3.326	56.370
	DCE	0.100	25 °C	-1.890	-	1.272	1.745	3.162	53.590
	AN	14.100	25 °C	-1.632	-	1.232	1.655	2.864	48.540
	THF	20.000	0 °C	-1.833	-	1.560	-	3.393	57.518
	DMSO	29.800	25 °C	-1.800	-	1.300	-	3.100	52.541
1b	DCM	1.000	0 °C	-1.708	-	1.250	1.617	2.958	50.125
	DCE	0.100	25 °C	-1.678	-	1.232	1.642	2.910	49.321
	AN	14.100	25 °C	-1.530	-	1.278	1.694	2.808	47.590
	THF	20.000	0 °C	-1.768	-	1.477	-	3.245	54.995
	DMSO	29.800	25 °C	-1.500	-	1.275	-	2.775	47.030
1c	DCM	1.000	0 °C	-1.490	-2.127	1.345	1.690	2.835	48.050
	DCE	0.100	25 °C	-1.420	-2.070	1.285	1.750	2.705	45.840
	AN	14.100	25 °C	-1.294	-2.102	1.290	1.690	2.584	43.790
	THF	20.000	0 °C	-1.700	-	1.500	-	3.200	54.242
	DMSO	29.800	25 °C	-1.230	-	1.340	-	2.570	43.550
1d	DCM	1.000	0 °C	-2.072	-	1.345	1.763	3.417	57.910
	DCE	0.100	25 °C	-2.000	-	1.303	1.696	3.303	55.980
	AN	14.100	25 °C	-1.780	-	1.268	1.692	3.048	51.660
	THF	20.000	0°C	-2.218	-	1.600	-	3.818	64.710
	DMSO	29.800	25 °C	-1.730	-	1.340	-	3.070	52.030
1e	DCM	1.000	0 °C	-1.418	-2.181	1.407	1.781	2.825	47.880
	DCE	0.100	25 °C	-1.418	-2.140	1.290	1.690	2.708	45.890
	AN	14.100	25 °C	-1.296	-2.104	1.272	1.680	2.568	43.500
	THF	20.000	0 °C	-1.918	-	1.540	-	3.458	58.610
	DMSO	29.800	25 °C	-1.150	-	1.310	-	2.460	41.689
1f**	DCM	1.000	0 °C	-1.454	-2.072	1.345	1.763	2.799	47.440
	DCE	0.100	25 °C	-1.500	-2.125	1.267	1.642	2.767	46.894
	AN	14.100	25 °C	-1.270	-2.064	1.296	1.712	2.566	43.490
	THF	20.000	0 °C	-1.900	-	1.400	-	3.300	55.930
	DMSO	29.800	25 °C	-1.210	-	1.350	-	2.560	43.390

* There is another peak in AN at E_p = 2.064(V), in DCE at E_p = 1.890(V), in DCM at E_p = 2.345(V).

** There is another peak in AN at E_p = 2.112(V), in DCE at E_p = 1.839(V), in DCM at E_p = 2.000(V).

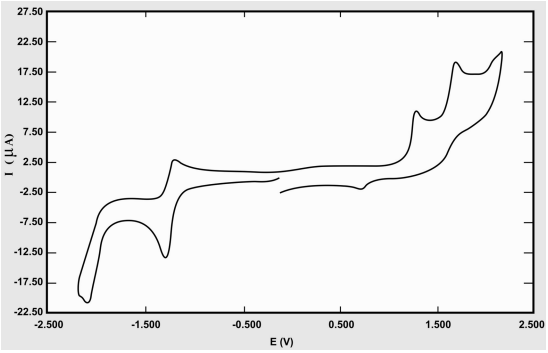
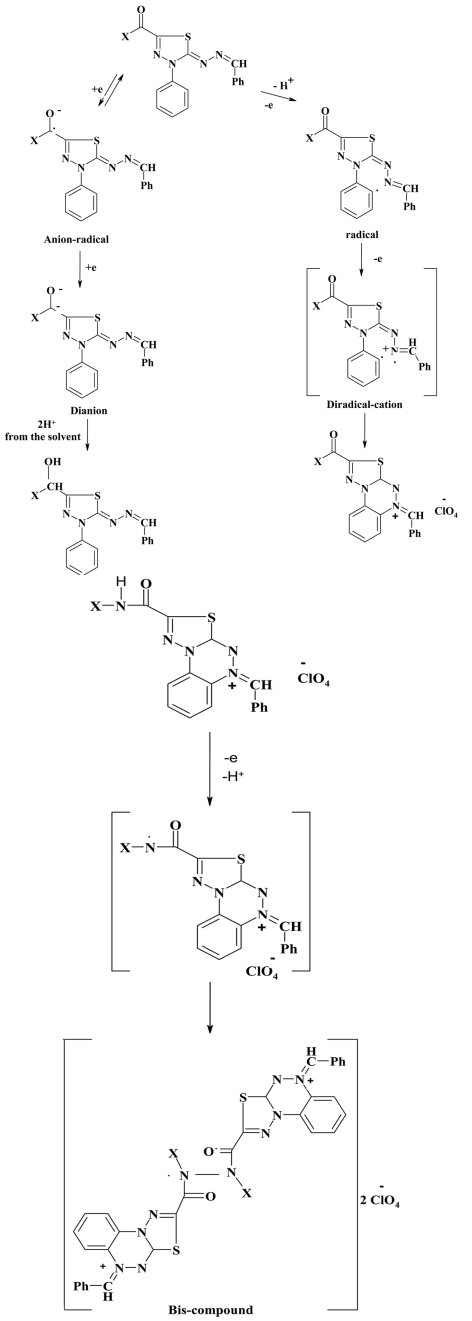


Fig. 1. CV-voltammogram of compound 1c in AN at Pt-electrode (scan rate = 100 mV/s; T = 25 °C).

3. Results and Dicussion

Cyclic voltammetric data listed in Table 1. Fig. 1 shows as an example the cyclic voltammogram of some investigated compounds. Compounds (1a-h) were oxidized in two irreversible one-electron processes following the well-known pattern of EC-mechanism. The first electron is followed by proton removal from the ortho-position in the N-phenyl ring forming the radical, this is 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 ring closure forming the corresponding cation. The formed cation can be stabilized in solution through its combination with a perchlorate anion from the medium. Compounds which contain the NH group (1a and 1f) undergo further oxidation. The NH is 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 from the values of ΔE_p and I_p^c / I_p^a. The increase of the withdrawing power of the substituent, makes 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.[21]

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

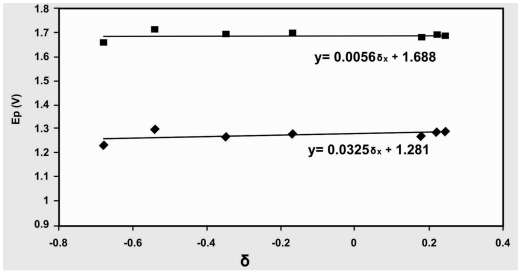


Fig (2a)

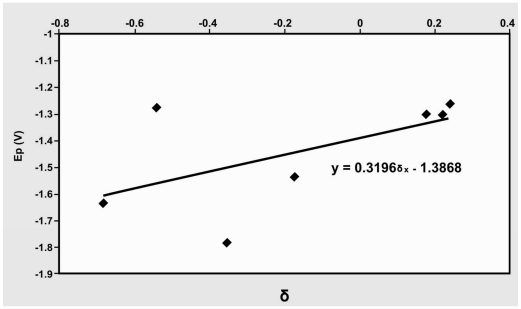


Fig (2b)

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

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 potentials of the substitued and unsubstituted compounds, respectively. Fig. 2(a), (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 C = O group which is in good agreement with the proposed reduction of adjacent C = O group.

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-

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

Solvent	Equation of series 1a -h
AN	$(E_p^{ox})_I = 0.0325\ \sigma_x + 1.2810$ (Oxidation)$_I$ $(E_p^{ox})_{II} = 0.0056\ \sigma_x + 1.6880$ (Oxidation)$_{II}$ $(E_p^{red}) = 0.3169\ \sigma_x - 1.3868$ (Reduction)
DCE	$(E_p^{ox})_I = 0.0336\ \sigma_x + 1.2876$ (Oxidation)$_I$ $(E_p^{ox})_{II} = 0.0545\ \sigma_x + 1.7150$ (Oxidation)$_{II}$ $(E_p^{red}) = 0.4513\ \sigma_x - 1.5468$ (Reduction)
DCM	$(E_p^{ox})_I = 0.0856\ \sigma_x + 1.3485$ (Oxidation)$_I$ $(E_p^{ox})_{II} = 0.0295\ \sigma_x + 1.7311$ (Oxidation)$_{II}$ $(E_p^{red}) = 0.5156\ \sigma_x - 1.5781$ (Reduction)
THF	$(E_p^{ox}) = 0.0226\ \sigma_x + 1.5033$ (Oxidation) $(E_p^{red}) = 0.1079\ \sigma_x - 1.874$ (Reduction)
DMSO	$(E_p^{ox}) = 0.0135\ \sigma_x + 1.3257$ (Oxidation) $(E_p^{red}) = 0.5028\ \sigma_x - 1.3257$(Reduction)

n-butylammonium perchlorate as supporting electrolyte. The voltammetric data are listed in Table 1. As shown by the data and voltammograms, compounds (1a-h), both oxidation and reduction of all the investigated compounds proceed identically in DCE, DCM and AN, they are oxidized in two irreversible one-electron processes to the diradical cation which in turn undergoes a follow up chemical reaction with ring closure; and are 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 the compounds which undergo a reversible or quasi-reversible reduction. In THF and DMSO (Fig. 3), the oxidation and also the reduction proceed in a 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 follows immediately. Going from DCE to DMSO (increasing the donor number from 0.1 to 29.8),[22] makes both the oxidation and reduction of these thiadiazoles easier. This behavior can be attributed to a solvation effect, as previously reported by many workers.[22-24] Fig. 4, represents the relationship between ΔE_p of compound 1d and the donor number of the solvents.

According to the Born-Haber cycle[25] 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:

$$F(\Delta E_p^{ox} - \Delta E_p^{red})$$
$$= F\{[E_p^{ox}(A) - E_p^{ox}(B)] - [E_p^{red}(A) - E_p^{red}(B)]\}$$
$$= F\{[E_p^{ox}(A) - E_p^{red}(A)] - [E_p^{ox}(B) - E_p^{red}(B)]\}$$

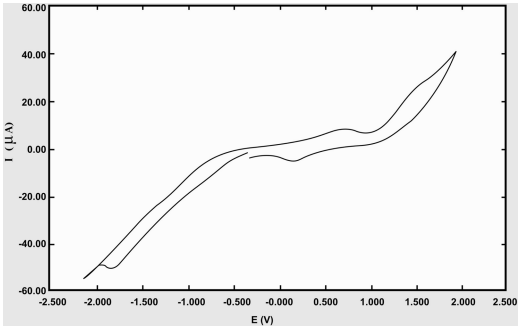


Fig. 3. CV-voltammogram of compound 1a in THF at Pt-electrode (scan rate = 100 mV/s; T = 25 oC).

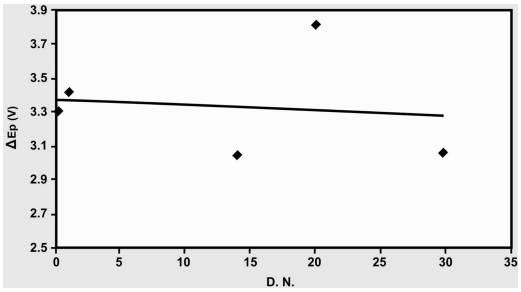


Fig. 4. Dependence of ΔEp of compound 1d on the donor number of the solvents.

$= -\delta\Delta G_{solv}(TD^{+\cdot}, A) + \delta\Delta G_{solv}(TD^{+\cdot}, B)$
$-\delta\Delta G_{solv}(TD^{-\cdot}, A) + \delta\Delta G_{solv}(TD^{-\cdot}, B)$
$= [\delta\Delta G_{solv}(TD^{+\cdot}, B) + \delta\Delta G_{solv}(TD^{-\cdot}, B)]$
$[\delta\Delta G_{solv}(TD^{+\cdot}, A) + \delta\Delta G_{solv}(TD^{-\cdot}, A)]$

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 changed the sum of the solvation energies is greater if the difference 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 in full agreement with rhe results obtained for hydrazyl.[20-22] This is in accordance with Gutmann's donor model.[22] 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 depends on the donor number of the solvent. This suggests that the 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 [20, 26, 27]. On the basis of substituent dependence it is expected that the oxidation potential will decrease, while the reduction potentiall 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 can be expressed as follows according to the principle of the cyclic process.[24]

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

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 in $\ddot{A}E_p$ follows the order:

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

i.e. the sum of the solvation energies for compounds in series (1a-h) increases in the order: ic 1e 1 g 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 agreement with the proposed mechanism. Assuming that the difference in the ionization potentials is small, the change of the solvation energies of the different investigated compounds in different solvents that obtained are listed in Table 3.

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

Solvent transition	$F(DE_p)_A - F(DE'_p)_A$ in two different solvents						
	1a	1b	1c	1d	1e	1f	1g
DCM DCE	F(164)	F(048)	F(130)	F(114)	F(117)	F(032)	F(054)
DCE AN	F(298)	F(237)	F(121)	F(255)	F(140)	F(201)	F(193)
DCM AN	F(462)	F(015)	F(251)	F(369)	F(257)	F(304)	F(247)

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