

Full Length Research Paper

Study of the electrochemical redox characteristics of some triazolopyrimidines

A. A. El Maghraby*, G. M. Abou Elenien and K. I. Shehata

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt.

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An electrochemical study related to the redox characteristics of Ethyl-3-acetyl-6-methyl-1,4-diphenyl-4,3a-dihydro-1,3,4-triazolino[3,4-a] pyrimidine-5-carboxylate ester and its derivatives (1a-f) and (2a-e) in nonaqueous solvents such as 1,2-dichloroethane (DCE), dichloromethane (DCM), acetonitrile (AN), dimethylsulphoxide (DMSO) and tetrahydrofuran (THF) using 0.1 mol dm⁻³ tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte at platinum, glassy carbon and gold electrodes, has been performed using cyclic voltammetry (CV). Controlled potential electrolysis (CPE) is also carried out to elucidate the course of different electrochemical reactions through the separation and identification of the intermediates and final electrolysis products. The redox mechanism is suggested and proved. It was found that all the investigated compounds in all solvents are oxidized in a single irreversible one electron donating process following the well known pattern of the EC-mechanism to give a dimer. On the other hand, these compounds are reduced in a single irreversible one electron step to form the anion radical, which is basic enough to abstract proton from the media forming the radical which undergoes tautomerization and then dimerization processes to give also another bis-compound through N-N linkage formation.

Key words: Cyclic voltammetry, oxidation, reduction, triazolopyrimidine, non-aqueous media, platinum electrode, glassy carbon electrode, gold electrode.

INTRODUCTION

Triazolopyrimidines and its derivatives are known to have many biological, pharmaceutical and analytical applications. Several triazolopyrimidine compounds have potential uses as a potent antibacterial drugs due to their higher antibacterial activity than some commercial anti-biotics against *Bacillus subtilis*, *Staphylococcus aureus* and *Salmonella typhi* at MIC (minimum inhibitory concentration) that is, 10 mg/ml (Eid and Abd El-Wahab, 2004; El-Agrody et al., 2000). Triazolopyrimidine compounds have an important potential role in cardiovascular therapeutics specially in platelet aggregation as an antiplatelet agent or anticoagulant (in the Japanese antiplatelet myocardial infarction study trapidil (triazolopyrimidine) 300 mg/day administered to more than 700 post-MI patients for about 1.5 years resulted in a significant reduction in CV events including CV death, reinfarction, and non fatal ischaemic stroke achieving successful advancement

more than aspirin. And in other cardiac diseases like angina, peripheral cardiac diseases and stroke (Yasue et al., 1999; Galassi et al., 1999; ASPECT Research Group, 1994; Behan and Storey, 2004; Hirayama et al., 2003; Mest, 1990) Because of this it was found worthwhile to investigate the redox characteristics of substituted triazolopyrimidines (1a-f) and (2a-e). These compounds were extensively studied using cyclic voltammetry in nonaqueous solvents. The number of electrons participating in each electrode reaction was determined using the coulometric 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 (Abdelhamide, 2005 unpublished work). All the synthesized compounds were purified by repeated crystallization, dried under reduced pressure and the purity was checked by thin layer chromatography. The measurements were carried out

*Corresponding author. E-mail: maghraby04@yahoo.com

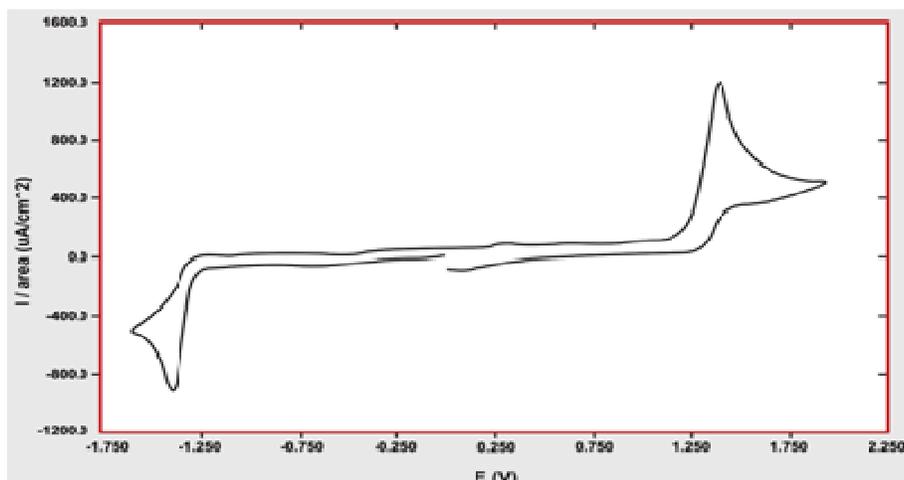


Figure 1. CV-voltammogram of compound 1a in (AN) at Pt-electrode (scan rate = 100mV/s; T = 25°C).

cobaltoceni-cobaltocene system (Abou-Elenien et al., 1993).

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 1a and 2d are reported here as examples. 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 cm²) 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.

The oxidation product of 1a: The ¹H NMR of the obtained oxidative product of 1a reveals that, the absence of the band corresponding to the C-H at carbon number four in pyrimidine ring at $\delta = 5.98$ compared with starting material 1a which gives a sharp band at $\delta = 5.91$ (S, 1H, CH). Also the mass spectral data gives $m^+/z = (738)$.

The Reduction product of 1a: The ¹H NMR of the obtained reductive product of 1a reveals that, the presence of the band corresponding to C-H at carbon number four in pyrimidine ring at $\delta = 5.98$ (S, 2H, 2CH) compared with starting material 1a which gives sharp band at $\delta = 5.9$ (S, 1H, CH). Also C-H of triazole ring appear at $\delta = 5.2$ (S, 2H, 2CH aliphatic). Also the mass spectra data gives $m^+/z = (742)$.

The oxidation product of 2d: The ¹H NMR of the obtained oxidative product of 2d reveals that, the absence of the band corresponding to the C-H at carbon number four in pyrimidine ring at $\delta = 5.82$ ppm compared with starting material 2d which gives a sharp band at $\delta = 5.62$ ppm (S, 1H, CH). Also the mass spectra

data gives $m^+/z = (780)$.

The Reduction product of 2d: The ¹H NMR of the obtained reductive product of 2d reveals that, the presence of the band corresponding to the C-H at carbon number four in pyrimidine ring at $\delta = 5.83$ ppm (S, 2H, 2CH) compared with starting material 1a which gives a sharp band at $\delta = 5.82$ ppm (S, 1H, CH). Also the C-H of triazole ring appear at $\delta = 5.5$ ppm (S, 2H, 2CH aliphatic). Also the mass spectra data gives $m^+/z = (784)$.

RESULTS AND DISCUSSION

Cyclic voltammetric data are listed in Tables (1) and (2). Figure (1) and (2) show as an example the cyclic voltammograms of some investigated compounds. Compounds (1a-f) and (2a-e) in all solvents are oxidized in a single irreversible one-electron donating process following the well known pattern of EC-mechanism; forming cation radical followed by a proton removal from the 4-position in the pyrimidyl ring forming the unstable intermediate (radical) which tautomerize and then dimerize to give the corresponding bis-compound (dimer) as in (scheme 1). On the other hand the reduction center in the investigated compounds seems to be the (C=N) in the triazole ring (Abou-Elenien et al., 2001a, b). Although the reported studies (O'Reilly and Elving, 1977; Battistuzzi et al., 1994; Navarro et al., 1995; Abou-Elenien et al., 2001c) gave the chance for dimerization through N-N coupling in the pyridine rings but in our case the presence of the more active center in the triazene ring favours the coupling through the atoms of this ring which have been proved in this work. Compounds (1a-f) and (2a-e) are reduced in an irreversible one electron gain to form the anion-radical, which is basic enough to abstract proton from the media (Abou-elenien, 1994; Abou-Elenien, 1991; Gutmann and Schmid, 1969; O'Reilly and Elving, 1977) forming the radical which undergoes tautomerization and then dimerization process to give also another bis-compound

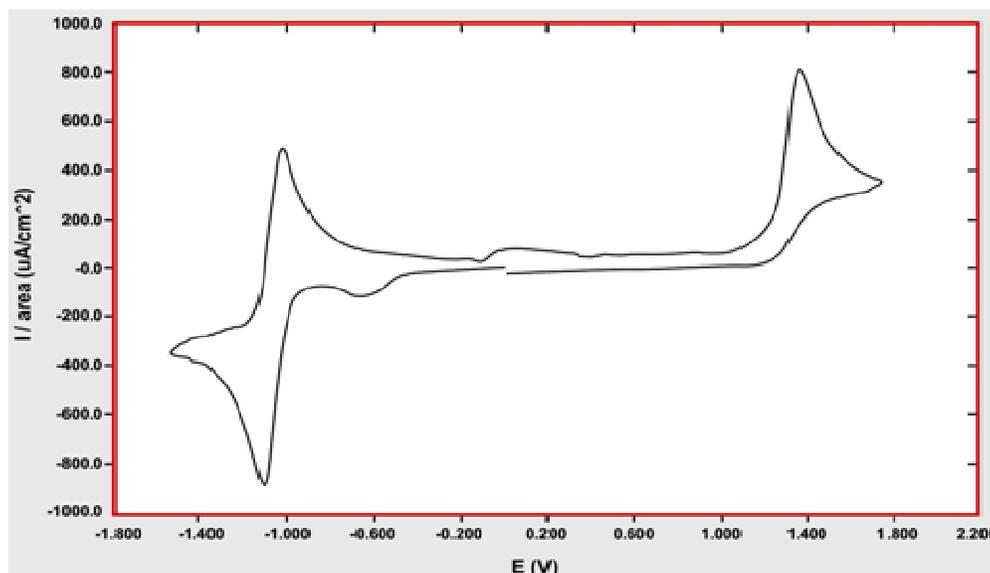


Figure 2. CV-voltammogram of compound 1c in (AN) at glassy C-electrode (scan rate = 100 mV/s; T = 25°C).

Table 1. Cyclic voltammetric data of compounds (1a-f) at pt, Glassy C and Au electrodes in different solvents (scan rate = 100 mv/s).

Compounds	Sol.	D.N.	Temp.	Electrode	Reduction	Oxidation	$\Delta E = E_p^{Ox} - E_p^{Red}$	Log K
					E_p (V)	E_p (V)		
1a	DCM	1.000	0°C	Pt	-1.493	1.529	3.022	51.219
				C	-1.482	1.528	3.010	51.016
				Au	-1.477	1.512	2.989	50.66
	DCE	0.100	25°C	Pt	-1.491	1.520	3.011	51.033
				C	-1.453	1.544	2.997	50.796
				Au	-1.462	1.520	2.982	50.54
	AN	14.100	25°C	Pt	-1.394	1.396	2.790	47.321
				C	-1.395	1.384	2.779	47.118
				Au	-1.385	1.378	2.763	46.897
	THF	20.000	0°C	Pt	-1.790	1.960	3.750	63.558
				C	-1.760	1.610	3.370	57.118
				Au	-1.750	1.770	3.520	59.660
	DMSO	29.800	25°C	Pt	-1.449	1.280	2.729	46.253
				C	-1.490	1.263	2.753	46.66
				Au	-1.435	1.440	2.875	48.728

through N-N linkage formation (Scheme 1). The stability of this anion-radical can be seen from the shape of the re-duction peak and also from the values of ΔE_p and I_p^c/I_p^a .

Substituent effect

The effect of substituents on the redox mode of an electroactive site can be illustrated by applying the well –

known modified Hammett equation of the form (Jaffe, 1953).

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

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 potentials of the substituted and unsubstituted compounds respectively. Figure 3a, b illustrate the Hammett equation correlations of the peak potentials of

Table 1. (continued)

Compound	Sol.	D.N.	Temp.	Electrode	Reduction	Oxidation	$\Delta E = E_p^{Ox} - E_p^{Red}$	Log K
					E_p (V)	E_p (V)		
1b	DCM	1.000	0°C	Pt	-1.758	1.540	3.298	55.898
				C	-1.707	1.526	3.233	54.796
				Au	-1.712	1.527	3.239	54.898
	DCE	0.100	25°C	Pt	-1.768	1.543	3.311	56.118
				C	-1.726	1.537	3.263	55.3
				Au	-1.791	1.534	3.325	56.355
	AN	14.100	25°C	Pt	-1.611	1.458	3.069	52.02
				C	-1.606	1.417	3.023	51.237
				Au	-1.595	1.393	2.988	50.643
	THF	20.000	0°C	Pt	-1.770	1.970	3.740	63.389
				C	-1.570	1.665	3.235	54.83
				Au	-1.410	1.780	3.190	54.067
	DMSO	29.800	25°C	Pt	-1.636	1.283	2.919	49.474
				C	-1.681	1.255	2.936	49.762
				Au	-1.646	1.399	3.045	51.609

Table 1. (Continued)

Compound	Sol.	D.N.	Temp.	Electrode	Reduction	Oxidation	$\Delta E = E_p^{Ox} - E_p^{Red}$	Log K
					E_p (V)	E_p (V)		
1c	DCM	1.000	0°C	Pt	-1.217	1.538	2.755	46.694
				C	-1.203	1.527	2.730	46.270
				Au	-1.212	1.522	2.734	46.338
	DCE	0.100	25°C	Pt	-1.147	1.577	2.724	46.169
				C	-1.134	1.560	2.694	45.66
				Au	-1.129	1.550	2.679	45.40
	AN	14.100	25°C	Pt	-1.387	1.411	2.798	47.016
				C	-1.100	1.370	2.470	41.864
				Au	-1.110	1.378	2.488	42.169
	THF	20.000	0°C	Pt	-1.200	1.600	2.800	47.457
				C	-1.400	1.750	3.150	53.389
				Au	-1.350	1.742	3.092	51.694
	DMSO	29.800	25°C	Pt	-1.150	1.318	2.468	41.830
				C	-1.133	1.249	2.382	40.372
				Au	-1.112	1.365	2.477	41.982

compounds (1a-f) for both oxidation and reduction processes. The equations of the regression lines obtained for the series (1a-f) are listed in Table 3.

It is obvious from equations in Table 3 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 electrooxidation. This fact implies that, there is more significant resonance interaction between the substituent and the reduction center (C=N group) in the triazole ring which is in good agree-

ment with the proposed reduction of adjacent (C=N 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-n-butylammonium perchlorate as supporting electrolyte. The effect of scan rate (V) on ΔE_p and I_p^c/I_p^a of the reversible reduction process is presented in Table (4), and Figure (2) represents as

Table 1. (Continued)

Compounds	Sol.	D.N.	Temp.	Electrode	Reduction	Oxidation	$\Delta E = E_{p,Red}^{Ox} - E_p$	Log K
					E_p (V)	E_p (V)		
1d	DCM	1.000	0°C	Pt	-1.800	1.454	3.254	55.152
				C	-1.774	1.442	3.216	54.508
				Au	-1.740	1.454	3.194	54.135
	DCE	0.100	25°C	Pt	-1.592	1.427	3.019	51.169
				C	-1.718	1.416	3.134	53.118
				Au	-1.710	1.429	3.139	53.203
	AN	14.100	25°C	Pt	-1.623	1.308	2.931	49.677
				C	-1.740	1.333	3.073	52.084
				Au	-1.653	1.305	2.958	50.135
	THF	20.000	0°C	Pt	-1.680	1.960	3.64	61.694
				C	-1.620	1.600	3.22	54.575
				Au	-1.420	1.740	3.16	53.219
	DMSO	29.800	25°C	Pt	-1.700	1.265	2.965	50.253
				C	-1.736	1.255	2.991	50.694
				Au	-1.733	1.429	3.162	53.592

Table (1). (continued)

Compounds	Sol.	D.N.	Temp.	Electrode	Reduction	Oxidation	$\Delta E = E_{p,Red}^{Ox} - E_p$	Log K
					E_p (V)	E_p (V)		
1e	DCM	1.000	0°C	Pt	-1.142	1.541	2.683	45.508
				C	-1.144	1.527	2.671	45.271
				Au	-1.126	1.522	2.648	44.88
	DCE	0.100	25°C	Pt	-1.087	1.550	2.637	44.711
				C	-1.084	1.552	2.636	44.203
				Au	-1.086	1.531	2.617	44.372
	AN	14.100	25°C	Pt	-1.038	1.412	2.45	41.525
				C	-1.053	1.372	2.425	41.101
				Au	-1.068	1.387	2.455	41.609
	THF	20.000	0°C	Pt	-1.720	1.910	3.63	61.52
				C	-1.530	1.640	3.17	53.728
				Au	-1.420	1.780	3.2	54.236
	DMSO	29.800	25°C	Pt	-1.018	1.351	2.369	40.152
				C	-1.002	1.336	2.338	39.626
				Au	-0.997	1.341	2.338	39.626

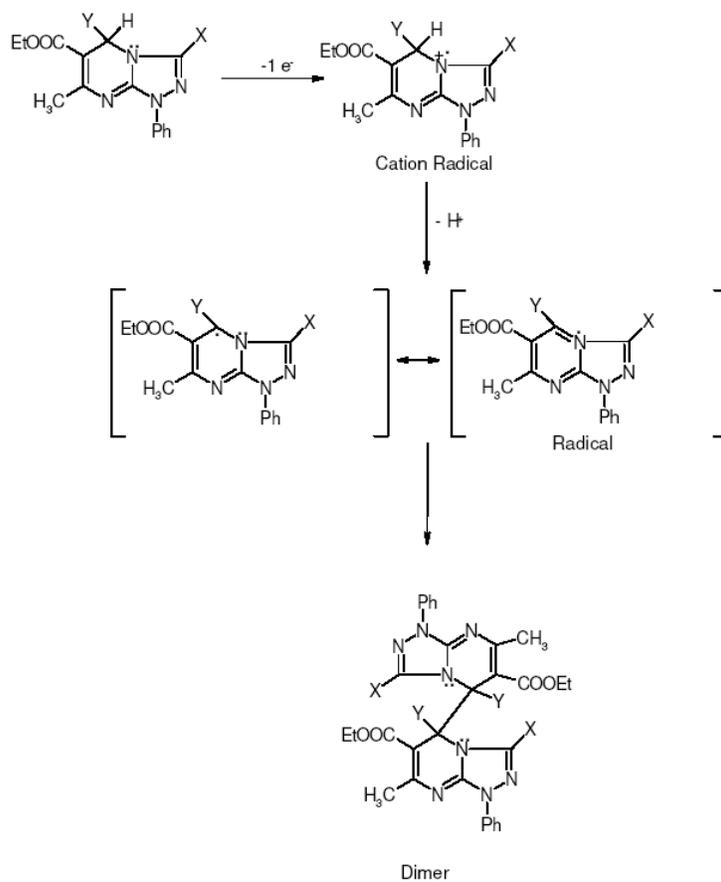
example the cyclic voltammogram of both oxidation and reduction of these compounds. The voltam-metric data are listed in Tables 1 and 2. As shown from the data and voltammograms (Figures 1 and 2) compounds (1a-f) show that in the other used non-aqueous solvents; (DCE, DCM, THF and DMSO) the redox mechanism of all the investigated compounds seems to be like that in AN in which the oxidation occurs in a single irreversible one electron donating processes; forming cation radical followed by a proton removal from the 4- position in the

pyrimidyl ring forming the unstable intermediate (radical) which tautomerize and then dimerize to give the corresponding bis-compound (dimer) as in (scheme 1).

On the other hand the reduction center in the investigated compounds seems to be the (C=N) in the triazole ring (Abou-Elenien et al., 2001a, 2001b). These compounds are reduced in an irreversible one electron gain to form the anion-radical, which is basic enough to abstract a proton from the media (Navarro et al., 1995; Abou-elenien, 1994; Abou-Elenien, 1991) forming the ra-

Table 1. (Continued)

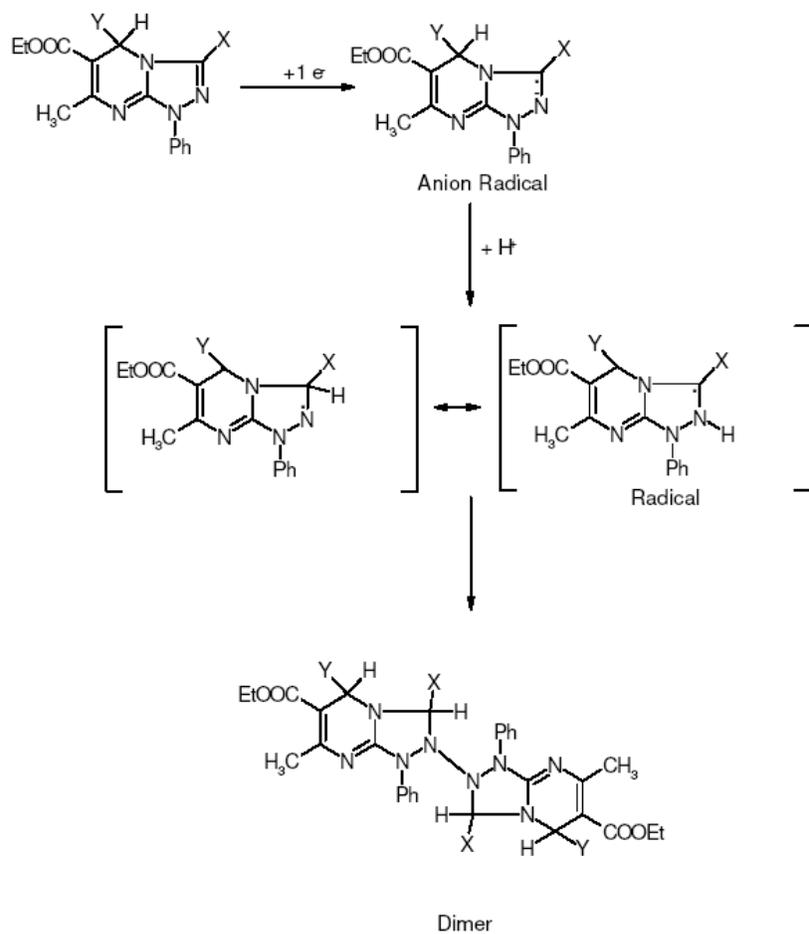
Compounds	Sol.	D.N.	Temp.	Electrode	Reduction	Oxidation	$\Delta E = E_p^{Ox} - E_p^{Red}$	Log K
					E_p (V)	E_p (V)		
1f	DCM	1.000	0°C	Pt	-1.794	1.530	3.324	56.338
				C	-1.692	1.508	3.2	54.237
				Au	-1.691	1.503	3.194	54.152
	DCE	0.100	25°C	Pt	-1.773	1.536	3.309	56.084
				C	-1.692	1.540	3.232	54.779
				Au	-1.748	1.533	3.281	55.609
	AN	14.100	25°C	Pt	-1.661	1.317	2.978	50.474
				C	-1.595	1.333	2.928	49.627
				Au	-1.600	1.353	2.953	50.05
	THF	20.000	0°C	Pt	-1.620	1.930	3.55	60.169
				C	-1.580	1.630	3.21	54.406
				Au	-1.420	1.780	3.2	54.236
	DMSO	29.800	25°C	Pt	-1.591	1.313	2.904	49.219
				C	-1.610	1.278	2.888	48.949
				Au	-1.614	1.254	2.868	48.609



Scheme 1 Oxidation

dical which undergoes tautomerization and then dimerization process to give also another bis-compound

through N-N linkage formation (Scheme 1). The reversibility and irreversibility of reduction can be obtained from



Scheme 1 Reduction

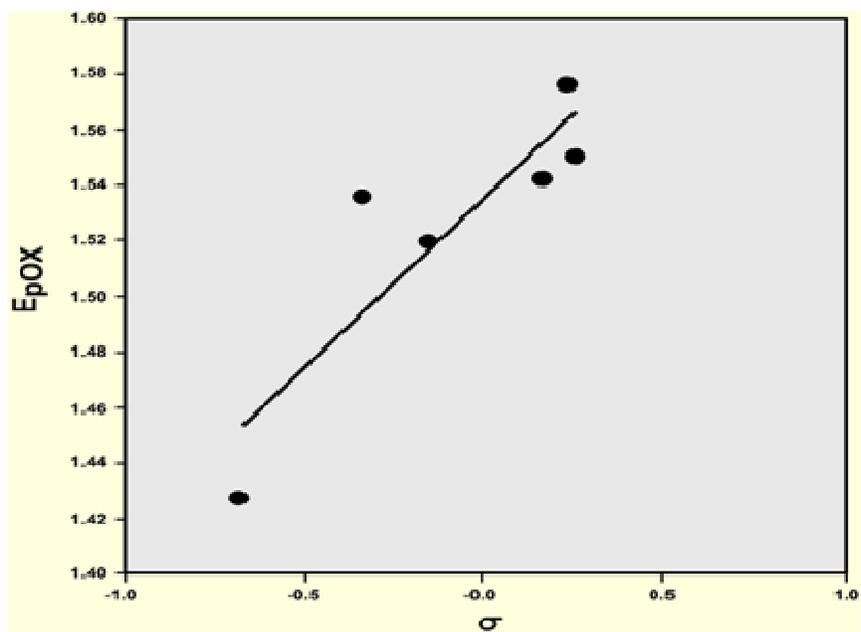


Figure 3a. Dependence of $E_p(ox)$ of compound (1a-f) in (DCE) on Hammett substitution constant (σ).

Table 2. Cyclic voltammetric data of compounds (2b-2e) at Pt, Glassy C and Au electrodes in different solvents (scan rate = 100 mv/s).

Compounds	Sol.	D.N.	Temp.	Electrode	Reduction	Oxidation	$\Delta E = E_p^{Ox} - E_p^{Red}$	Log K
					E_p (V)	E_p (V)		
2b	DCM	1.000	0°C	Pt	-1.648	1.446	3.094	51.219
				C	-1.568	1.417	2.985	51.016
				Au	-1.620	1.389	3.009	50.660
	DCE	0.100	25°C	Pt	-1.590	1.435	3.025	51.034
				C	-1.545	1.420	2.965	50.796
				Au	-1.585	1.429	3.014	50.542
	AN	14.100	25°C	Pt	-1.508	1.327	2.835	47.321
				C	-1.449	1.325	2.774	47.118
				Au	-1.472	1.309	2.781	46.898
	THF	20.000	0°C	Pt	-1.120	1.600	2.720	63.559
				C	-1.110	1.580	2.690	57.118
				Au	-1.102	1.590	2.692	59.660
	DMSO	29.800	25°C	Pt	-1.554	1.217	2.771	46.254
				C	-1.550	1.203	2.753	46.660
				Au	-1.536	1.330	2.866	48.728

Table 2. (Continued)

Compounds	Sol.	D.N.	Temp.	Electrode	Reduction	Oxidation	$\Delta E = E_p^{Ox} - E_p^{Red}$	Log K
					E_p (V)	E_p (V)		
2c	DCM	1.000	0°C	Pt	-1.575	1.502	3.077	52.152
				C	-1.518	1.481	2.999	50.830
				Au	-1.508	1.462	2.970	50.508
	DCE	0.100	25°C	Pt	-1.558	1.496	3.054	51.762
				C	-1.461	1.490	2.951	50.017
				Au	-1.508	1.462	2.970	49.796
	AN	14.100	25°C	Pt	-1.411	1.345	2.756	46.712
				C	-1.402	1.335	2.737	46.389
				Au	-1.390	1.327	2.717	46.050
	THF	20.000	0°C	Pt	-1.110	1.670	2.780	46.949
				C	-1.100	1.680	2.780	47.118
				Au	-1.120	1.640	2.760	46.779
	DMSO	29.800	25°C	Pt	-1.459	1.219	2.678	45.389
				C	-1.476	1.240	2.716	46.034
				Au	-1.455	1.207	2.662	45.118

the presence of the reverse peaks in the cyclic voltammograms of compound 1c and 1e Figure (2) and from the variation of the values of ΔE_p and I_p^{red}/I_p^{ox} with scan rate (Table 4). The results show that the reduction process of both 1c and 1e satisfy the requirements of quasi-reversible mechanism in the three solvents at least at low scan rates. The substituents in these compounds will stabilize "to some extent" the intermediate. The formation of the radical-anion during the reduction has been proved by others (Iversen, 1972; Zhang, 1991; Bard and Faulkner, 1980). The verification and adjustment of the

redox scheme will be established through controlled potential electrolysis which gives us the possibility to separate and identify the final oxidation and reduction products. The analysis and the spectral data of the separated products are coinciding with the structure of the products. No difference appears in the redox mode of these compounds (series 1 and 2) by using Pt, glassy C or Au electrodes. Generally it appears that, the peak current in the oxidation process is more or less higher at the Au-electrode than at the Pt-electrode which may be attributed to the complexing ability of the Au-electrode

Table 2. (continued)

Compounds	Sol.	D.N.	Temp.	Electrode	Reduction	Oxidation	$\Delta E = E_p^{ox} - E_p^{red}$	Log K
					E_p (V)	E_p (V)		
2d	DCM	1.000	0°C	Pt	-1.559	1.45	3.009	50.999
				C	-1.504	1.457	2.961	50.186
				Au	-1.518	1.458	2.976	50.406
	DCE	0.100	25°C	Pt	-1.508	1.455	2.963	50.219
				C	-1.454	1.444	2.898	49.118
				Au	-1.518	1.458	2.976	49.898
	AN	14.100	25°C	Pt	-1.412	1.341	2.753	46.660
				C	-1.381	1.304	2.685	45.508
				Au	-1.395	1.345	2.740	46.44
	THF	20.000	0°C	Pt	-1.490	1.685	3.175	53.898
				C	-1.500	1.690	3.190	53.898
				Au	-1.300	1.680	2.980	50.508
	DMSO	29.800	25°C	Pt	-1.454	1.286	2.740	46.440
				C	-1.458	1.277	2.735	46.356
				Au	-1.450	1.370	2.820	47.796

Table 2. (Continued)

Compounds	Sol.	D.N.	Temp.	Electrode	Reduction	Oxidation	$\Delta E = E_p^{ox} - E_p^{red}$	Log K
					E_p (V)	E_p (V)		
2e	DCM	1.000	0°C	Pt	-1.535	1.490	3.025	51.270
				C	-1.501	1.479	2.980	50.508
				Au	-1.499	1.467	2.966	50.305
	DCE	0.100	25°C	Pt	-1.489	1.484	2.973	50.389
				C	-1.518	1.484	3.002	50.881
				Au	-1.499	1.467	2.966	49.864
	AN	14.100	25°C	Pt	-1.427	1.351	2.778	47.05
				C	-1.386	1.349	2.735	46.356
				Au	-1.369	1.358	2.727	46.219
	THF	20.000	0°C	Pt	-1.600	1.590	3.190	54.067
				C	-1.650	1.680	3.330	56.440
				Au	-1.670	1.720	3.390	57.457
	DMSO	29.800	25°C	Pt	-1.451	1.250	2.701	45.779
				C	-1.426	1.263	2.689	45.576
				Au	-1.430	1.360	2.790	47.287

with the oxidation product of these compounds (Wandlowski et al., 1993; Gabert and Baumgartel, 1985a; 1985b).

Increasing the donor number (DN) (Gutmann, 1973) of the solvent makes both the oxidation and reduction of the triazolopyrimidines easier (Tables 1 and 2). This behavior can be attributed to the solvation effect, as already reported by many workers (Nelson and Iwamoto, 1961; Gutmann and Schmid, 1969).

According to the Born-Haber cycle (Case, 1965), the E_p

values for one triazolopyrimidine in two different solvents A and B and the solvation energies of the corresponding ions can be derived as follows:

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

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

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

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

Table 3. The Linear relation parameter between Hammett constant and potential for compounds (1a-f)

Solvent	Pt	C	Au
AN	$(E_p^{ox})_l = 0.130 \sigma_x + 1.392$ $(E_p^{red}) = 0.394 \sigma_x - 1.414$	$(E_p^{ox})_l = 0.062 \sigma_x + 1.374$ $(E_p^{red}) = 0.597 \sigma_x - 1.356$	$(E_p^{ox})_l = 0.081 \sigma_x + 1.374$ $(E_p^{red}) = 0.515 \sigma_x - 1.352$
DCE	$(E_p^{ox})_l = 0.123 \sigma_x + 1.538$ $(E_p^{red}) = 0.448 \sigma_x - 1.432$	$(E_p^{ox})_l = 0.104 \sigma_x + 1.530$ $(E_p^{red}) = 0.544 \sigma_x - 1.415$	$(E_p^{ox})_l = 0.097 \sigma_x + 1.525$ $(E_p^{red}) = 0.537 \sigma_x - 1.435$
DCM	$(E_p^{ox})_l = 0.077 \sigma_x + 1.529$ $(E_p^{red}) = 0.576 \sigma_x - 1.477$	$(E_p^{ox})_l = 0.079 \sigma_x + 1.517$ $(E_p^{red}) = 0.541 \sigma_x - 1.447$	$(E_p^{ox})_l = 0.067 \sigma_x + 1.513$ $(E_p^{red}) = 0.514 \sigma_x - 1.442$
THF	$(E_p^{ox})_l = 0.021 \sigma_x + 1.800$ $(E_p^{red}) = 0.160 \sigma_x - 1.614$	$(E_p^{ox})_l = 0.101 \sigma_x + 1.659$ $(E_p^{red}) = 0.165 \sigma_x - 1.560$	$(E_p^{ox})_l = 0.015 \sigma_x + 1.767$ $(E_p^{red}) = 0.070 \sigma_x - 1.455$
DMSO	$(E_p^{ox})_l = 0.054 \sigma_x + 1.307$ $(E_p^{red}) = 0.550 \sigma_x - 1.370$	$(E_p^{ox})_l = 0.0280 \sigma_x + 1.275$ $(E_p^{red}) = 0.581 \sigma_x - 1.388$	$(E_p^{ox})_l = -0.021 \sigma_x + 1.369$ $(E_p^{red}) = 0.609 \sigma_x - 1.363$

Table 4. CV-voltammetric data for the compounds (1c) and (1e) in different solvents at Pt, glassy C and Au electrodes (at different scan rates).

Scan rate (mV/sec)	1c on Pt electrode								1c on glassy C electrode							
	AN		DCE		DCM		DMSO		AN		DCE		DCM		DMSO	
	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a
30	117	1	138	1.135	152	1.013	126	1.2	112	1.1	128	0.83	126	1.034	155	1.24
50	112	0.95	168	1.28	155	1.03	134	0.9	97	1.17	143	0.946	143	1.143	259	1.08
70	112	0.98	173	1.236	172	0.984	90	1.07	97	0.97	153	0.88	149	1.27	174	0.93
90	121	0.976	189	1.243	193	0.986	154	1.16	97	1.09	143	0.865	166	1.29	135	1.13
100	97	1	178	1.013	188	0.84	110	0.82	92	1.02	163	1.095	187	0.866	98	1.2
200	121	1	229	1.19	234	0.94	130	1.02	107	1	204	0.893	206	1.28	106	1
300	91	1	275	1.15	265	0.91	126	0.98	97	0.987	219	1.178	211	1.14	118	1.012
400	132	1.03	280	1.142	290	1.047	138	0.97	102	1	244	0.973	252	1.03	106	1.077
500	131	1.02	320	1.087	316	0.905	138	0.9	102	1	249	0.964	263	1.04	118	0.94

Where TD represents the triazolopyrimidine 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 Tables (1) and (2), ΔE_p for all the investigated triazolopyrimidines (1a-f and 2a-e) decreased when the solvent changed from 1,2-dichloroethane to acetonitrile; i.e. the sum of the

solvation energies increased which is in full agreement with the results obtained for hydrazyl (Gutmann, 1973; Abou-Elenien, 1993). This is in accordance with Gutmann's donor model (Gutmann, 1973). In all cases there is a linear relationship between the electrochemical

Table 4. (continued)

Scan rate (mV/sec)	1 _c on Au electrode								1 _e on Pt electrode							
	AN		DCE		DCM		DMSO		AN		DCE		DCM		DMSO	
	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a
30	96	1.26	106	1.083	137	0.7			97	1.15	122	1	119	1.071	55	1.34
50	110	1.16	114	1.012	137	1.096			92	1.04	143	0.94	146	1.05	92	1.35
70	98	1.08	133	1.052	154	1.1			102	0.842	147	0.853	174	0.97	81	1.3
90	105	1.05	133	1.053	160	1.103			82	1.014	163	1.025	183	1.035	133	1.15
100	106	1.1	143	1.06	173	0.85			92	1.04	163	1	192	1.32	123	1.7
200	96	0.97	164	1.093	204	0.85			102	1.013	204	0.988	238	1.14	112	1.33
300	96	0.97	179	1.053	214	0.9			102	1.013	224	0.94	270	1	123	1.38
400	109	1	183	1.03	214	0.825			112	0.98	245	0.95	297	1.17	133	1
500	105	0.97	197	1	234	0.933			117	0.99	270	0.933	300	0.88	138	1.1

Table 4. (continued)

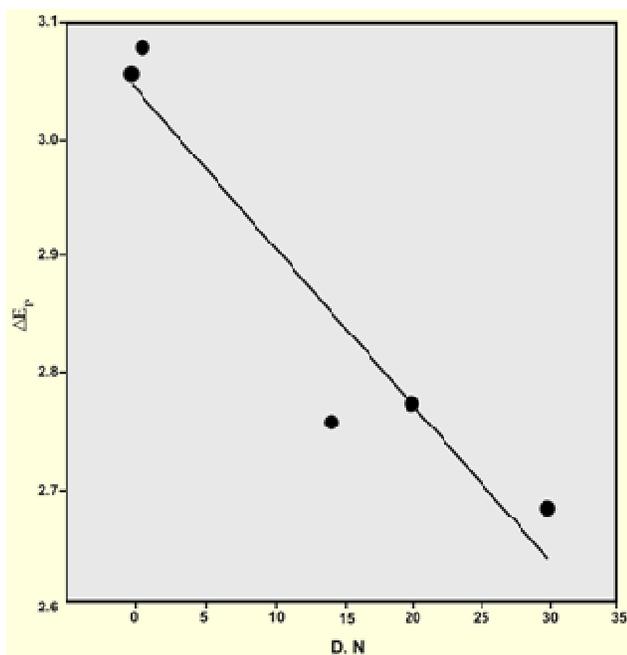
Scan rate (mV/sec)	1 _e on glassy C electrode								1 _e on Au electrode							
	AN		DCE		DCM		DMSO		AN		DCE		DCM		DMSO	
	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a	ΔE_p (mV)	I_p^c/I_p^a
30	137	1.029	171	1.13	166	1.13	28	1.63	86	0.95	144	1.296	120	1	41	1.35
50	97	0.898	155	1.32	149	1.29	46	1.63	87	1	155	1.25	149	0.98	102	1.26
70	87	0.952	178	1.34	172	1.14	65	1.63	92	0.971	144	1.375	149	1	97	1.45
90	87	1	167	1.38	183	1.36	83	1.6	87	0.919	172	1.44	167	1.2	77	1.56
100	92	1.02	155	1.447	211	1.34	92	1.64	92	1.047	163	1.11	172	1.18	76	1.56
200	92	1	195	1.44	240	1.1	99	1.63	87	0.957	188	1.14	195	1.19	118	1.38
300	102	0.975	223	1.346	264	1.27	117	1.63	87	1.02	195	1.25	212	1.12	138	1.3
400	97	0.952	211	1.375	292	1.143	134	1.63	87	0.897	252	1.14	234	1.15	113	1
500	107	0.964	252	1.29	314	1.2	130	1.63	92	0.9	241	1.38	235	1.02	118	1.5

Table 5. Difference in solvation energies of compounds (1a-f) in different solvents.

Solvent transition	Electrode	$F(\Delta E_p)_A - F(\Delta E_p)_A$ in two different solvents					
		1a	1b	1c	1d	1e	1f
DCM→DCE	Pt	F(11)	F(13)	F(31)	F(235)	F(46)	F(15)
	C	F(13)	F(30)	F(36)	F(82)	F(35)	F(32)
	Au	F(7)	F(86)	F(55)	F(55)	F(31)	F(87)
DCE→AN	Pt	F(221)	F(242)	F(74)	F(88)	F(187)	F(331)
	C	F(218)	F(240)	F(224)	F(61)	F(211)	F(304)
	Au	F(219)	F(337)	F(191)	F(181)	F(162)	F(328)
DCM→AN	Pt	F(232)	F(229)	F(43)	F(323)	F(233)	F(346)
	C	F(231)	F(210)	F(260)	F(143)	F(246)	F(272)
	Au	F(226)	F(251)	F(246)	F(236)	F(193)	F(241)

Table 6. Difference in solvation energies of compounds (2a-e) in different solvents.

Solvent transition	Electrode	$F(\Delta E_p)_A - F(\Delta E_p)_A$ in two different solvents				
		2a	2b	2c	2d	2e
DCM→DCE	Pt	F(11)	F(69)	F(23)	F(46)	F(52)
	C	F(13)	F(20)	F(48)	F(63)	F(22)
	Au	F(7)	F(5)	F(32)	F(32)	F(24)
DCE→AN	Pt	F(221)	F(190)	F(298)	F(210)	F(195)
	C	F(218)	F(191)	F(214)	F(213)	F(267)
	Au	F(219)	F(233)	F(221)	F(204)	F(215)
DCM→AN	Pt	F(232)	F(259)	F(321)	F(256)	F(247)
	C	F(231)	F(211)	F(262)	F(276)	F(245)
	Au	F(226)	F(233)	F(253)	F(236)	F(239)

**Figure 4.** Dependence of ΔE_p of compound 2d on the number of the solvents (D.N.).

parameters (E_p , ΔE_p and $\log k$) and the donor number (Figure 4).

Accordingly, the sum of the solvation energies of a particular triazolopyrimidine in a given solvent depends 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 triazolopyrimidines in THF and DMSO is due to perturbation of the solvent by, for example, formation of an ion pair (Abou-Elenien, 1993; Patai, 1967; Searles Jr. and Tamres, 1967). Also, the solvation of the formed ion radical of two different substituted triazolopyrimidines in the same solvent can be expressed as follows according to the principle of the cyclic process (Gutmann and Schmid, 1969).

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

$$- [\delta\Delta G_{\text{solv}}(1c)^{+\bullet} + \delta\Delta G_{\text{solv}}(1c)^{-\bullet}]$$

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.

Tables (1 and 2) show a regular increase in ΔE_p for the compounds using different solvents.

Taking in consideration the allowed experimental error, the increase follows the order:

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

$$(\Delta E_p)_{2d} < (\Delta E_p)_{2a} < (\Delta E_p)_{2e} < (\Delta E_p)_{2c} < (\Delta E_p)_{2b}$$

$$1f > 1b > 1d > 1a > 1c > 1e; 2b > 2c > 2e > 2a > 2d$$

This can be explained from the fact that the substituents are far away from the oxidation center of the i.e. the sum of the solvation energies for compounds in the two series (1a-f) and (2a-e) increase in the order: (Tables 5 and 6) molecules due to tautomerization process see (scheme1), 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 is small, the change of the solvation energies of the different investigated compounds in different solvents which obtained are listed in Tables (5) and (6). 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.

Conclusion

The electrochemical redox characteristics of some triazolopyrimidines of 1a-f and 2a-e are studied and the redox mechanism is suggested and proved. All compounds are oxidized in a single irreversible one electron donating process following EC-mechanism to give a dimer. They are reduced in a single irreversible one electron step gives anion radical which abstract a proton from the media forming the radical which tautomerize and dimerizes through N-N linkage formation.

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