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Oxidative Ring Cleavage of 4-(4-R-phenyl)-1,2,4-triazolidine-3,5-diones: Electrochemical Behavior and Kinetic Study

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Cyclic voltammetry results as a diagnostic technique for electrochemical oxidation of 4-(4-R-phenyl)-1,2,4-triazolidine-3,5-diones (**1-5**) are reported and discussed. The results indicate that the electrochemically generated 4-(4-R-phenyl)-4*H*-1,2,4-triazole-3,5-diones (**1ox-5ox**) are unstable and participate in oxidative ring cleavage. In this study, the effect of different parameters such as pH, 4-phenylurazole concentration, solvent, temperature, substitute effect and time window of chosen electrochemical method have been studied. Also, the transfer coefficient, α, exchange current density, J_0, the formal potential, $E^{0'}$ and diffusion coefficient, D, of 4-phenylurazole (**1**) have been calculated. In addition, the observed homogeneous rate constants of oxidative ring cleavage of 4-phenylurazole derivatives were estimated by comparing the experimental cyclic voltammetric responses with digital simulated results.
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Electrochemistry provides very versatile means for the electrosynthesis, mechanistic and kinetic studies.[1–8] Among electrochemical methods, it is known that cyclic voltammetry is a powerful technique for investigation of electrochemical reactions that are coupled with chemical reactions.[9,10] Urazole as an important biochemical reagent and a prebiotic compound acting as the precursor to uracil has been used in studies of the origin of life.[11,12] Effectiveness of urazole as an herbicide against weeds, production of anti-tumor drugs,[13,14] the stabilizer in milk, and insecticides have been confirmed. Some urazole derivatives were found to be potent cytotoxic agents in murrain and human cancer cell lines and also reduce DNA synthesis considerably with moderate reduction in RNA synthesis.[15] The comparison between electrochemical and bioactive properties with some evidence of relationship, bears a great significance.[16] The propensity of a molecule to donate or accept an electron in solution is measured by its standard redox potential and knowledge of standard redox potential is fundamental to understanding the chemical and biological electron-transfer reactions.[17,18] Furthermore, numerous fundamental and harmful processes in living cells, such as cytochrome P450 catalyzed oxidation in liver microsomes, are governed and stimulated by redox reaction.[19] The oxidation of urazole derivatives has previously been studied in different media.[20–24] It is reported that, the high reactivity of these compounds is due to the simultaneous presence of both carbonyl and azo moieties.[24] Also, the oxidative cleavage pathway which leading to the various products was discussed.[24] In addition, in our previous paper, it is discovered that the stability of electrogenerated 4-R-4*H*-1,2,4-triazole-3,5-dione (**1ox-5ox**) depended on the media conditions.[25] So investigation the effect of different parameters on the stability of electrogenerated 4-R-4*H*-1,2,4-triazole-3,5-dione (**1ox-5ox**) is useful to have a success chemical or electrochemical synthesis via oxidation of urazoles and seems to be interesting for all workers who deal with these compounds. Therefore, in this work, the anodic oxidative ring cleavage of 4-(4-R-phenyl)-1,2,4-triazolidine-3,5-diones (**1-5**) has been studied in aqueous solution and the effect of different parameters such as pH, 4-phenylurazole concentration, solvent, temperature, substitute effect and time window of chosen electrochemical method have been taken in order to more understanding about instability of 4-R-4*H*-1,2,4-triazole-3,5-dione (**1ox-5ox**). Also, the transfer coefficient, α, exchange current density, J_0, formal potential, $E^{0'}$, diffusion coefficient, D, and some thermodynamic parameters for oxidation-reduction reaction of 4-phenylurazole (**1**) have been calculated. In addition, the observed homogeneous rate constants of oxidative ring cleavage of 4-(4-R-phenyl)-1,2,4-triazolidine-3,5-diones (**1-5**) were estimated by comparing the experimental cyclic voltammetric responses with digital simulated results.

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Experimental

Apparatus and reagents.— Cyclic voltammetry and chronoamperometry were performed using an Autolab model PGSTAT 30 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disk (1.8 mm diameter) and a platinum wire was used as the counter electrode. The working electrode potentials were measured vs. Ag/AgCl. More details are described in our previous paper.[26] Urazole derivatives were synthesis according to previously reported producers.[27,28] Digital simulation was performed using the DIGIELCH simulation software version 2.0.[29] All solutions in electroreduction studies were deoxygenated by bubbling pure nitrogen.

The peak current ratios (I_p^C/I_p^A) were determined using the following equation.

$$I\text{pc}/I\text{pa} = (I\text{pc})_0/I\text{pa} + 0.485(I\text{sp})_0/I\text{pa} + 0.086$$

where $(I\text{pc})_0$ and $(I\text{sp})_0$ are cathodic peak current and "*switching potential*" current respect to the zero current, respectively. *I*pc and *I*pa have their usual meanings.

Results and Discussion

The effect of potential scan rate.— The electrochemical study of 4-phenylurazole (**1**) in the aqueous phosphate buffer (c = 0.2 M, pH 2.0), at a glassy carbon electrode has been performed using cyclic voltammetry at different scan rates (Fig. 1).

As shown in Fig. 1 in low scan rate (100 mV/s), the cyclic voltammogram exibits the feature of an irreversible electron-transfer process with an anodic peak (A_1) at 0.70 V vesus Ag/AgCl which corresponds to the transformation of 4-phenylurazole (**1**) to 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (**1ox**) (Scheme 1).[25] It is seen that, proportionally to the augmentation of potential sweep rate, the peak current ratio (I_{pC1}/I_{pA1}) increases. The ratio of I_{pC1}/I_{pA1} and the anodic peak current function, $I_{pA1}/v^{1/2}$, versus the potential scan rate are also shown in Fig. 1. It is observed that, proportional to the increasing of the potential sweep rate I_{pC1}/I_{pA1} increases gradually. In the cyclic voltammetric method, the potential scan rate is an effective experimental parameter which can be used to control τ, a measure of the period during which a stable electroactive species can communicate with the electrode. By increasing the scan rate this characteristic time is limmited compared

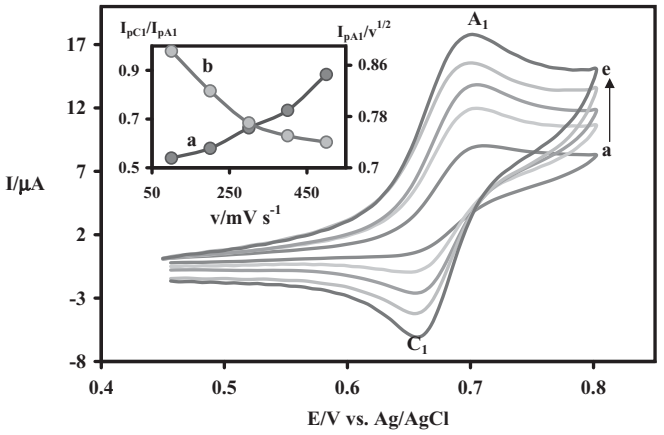


Figure 1. Cyclic voltammograms of 0.5 mM 4-phenylurazole (**1**) in phosphate buffer ($c = 0.2$ M, pH = 2.0) solution at different scan rates at a glassy carbon electrode. Scan rates from (a) to (e) are: 100, 200, 300, 400 and 500 mV/s. Inset: Variation of the peak currents ratio (I_{pC1}/I_{pA1}) (curve a) and anodic peak current function, $I_{pA1}/v^{1/2}$ (curve b) versus scan rate, $T = 25 \pm 1$°C.

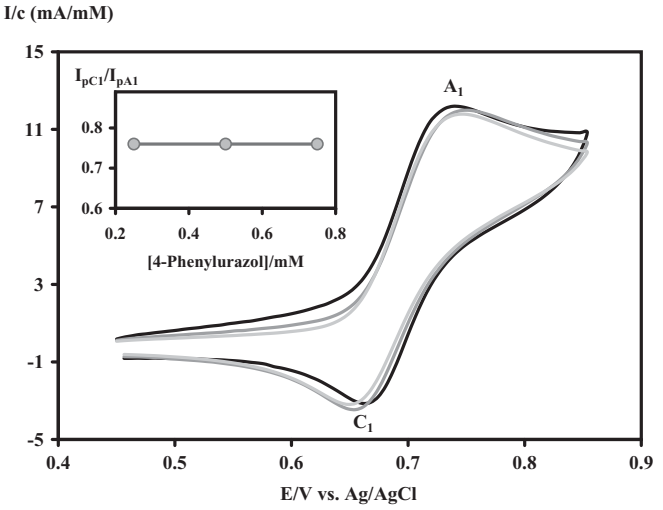


Figure 2. Normalized cyclic voltammograms (I/c) of 4-phenylurazole (**1**) in phosphate buffer ($c = 0.2$ M, pH = 2.0) solution at various concentrations (c = 0.25, 0.5 and 0.75 mM), at a glassy carbon electrode. Scan rate: 200 mV/s, $T = 25 \pm 1$°C.

to t, which t is the charactristic lifetime of a coupled chemical reaction. This behavior is fully confirmed by plotting the variation $I_{pA}/v^{1/2}$ vesus the potential scan rate. Under the above conditions, the plots of $I_{pA}/v^{1/2}$ vesus the potential scan rate is a characteristic shape typical of an E_rC_i mechanism established by Nicholson and Shain.[30]

*The effect of concentration of 4-phenylurazole (**1**).*— Electrochemical oxidation of 4-phenylurazole (**1**) has been studied in various concentrations. Fig. 2 shows normalized cyclic voltammograms of **1** at various concentrations. Normalization was performed by dividing the current on concentration (I/c vs. µA/mM). As can be seen in Fig. 2 the peak current ratio (I_{pC1}/I_{pA1}) is constant and independent to concentration of **l**. This confirms EC mechanism for electrochemical oxidation of 4-phenylurazole and rejects a second order reaction such as dimerization of **l** and oxidation form of **l** (**1ox**).

The effect of solvent and pH.— Fig. 3 shows the cyclic voltammograms of **l** in 0.1 M HCl containing various amount of acetonitrile (AN). It is observed that proportional to increasing of AN percent in mixture, the I_{pC1}/I_{pA1} ratio increases. In fact, proportional to increasing of AN percent, the rate of chemical reaction in EC mechanism decreases. This behavior can be depended on the water amount or hydroxide ion concentration. Actually, the acidity and basicity of solvent have a significant influence on the following chemical reaction. This behavior is related to decrease in solvent basicity arising decrease in donor number of mixture. Water has DN = 33, the addition of amount of AN with DN = 14.1 decreases the donor number of mixture and abstraction of proton.[31]

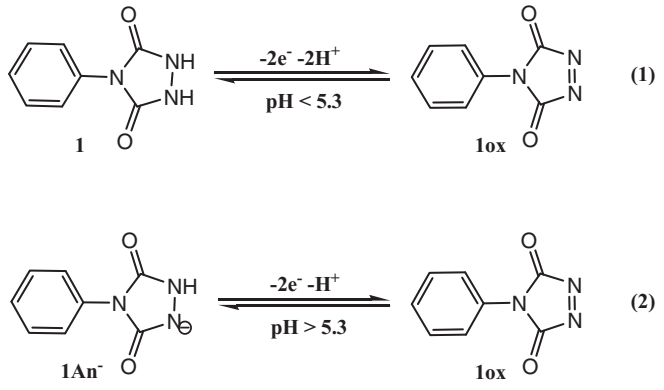
On the basis of these results, it is appeared that hydroxyl ion is the main driving force of the coupled chemical reaction in the *EC* mechanism. It is suggested that the observed instability of **1ox** corresponds to the nucleophilic attack of hydroxyl ion of the solution.

Fig. 4 shows the effect of pH solution on the voltammetric behavior of **1** at a glassy carbon electrode surface in AN/buffer solution in a pH range of 3.0–7.0.

It was found that the potential for peak A_1 (E_{pA1}) shifted to the negative potentials by increasing pH. This is expected because of the participation of proton(s) in the oxidation reaction of **1** to 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (**1ox**).

The anodic peak potential (E_{pA1}), is given by:

$$E'_{pA} = E_{pA(pH=0)} - (2.303\, mRT/2F)\text{pH} \qquad [1]$$



Scheme 1. Electrochemical oxidation of 4-phenylurazole (**1**) in different ranges of pH.

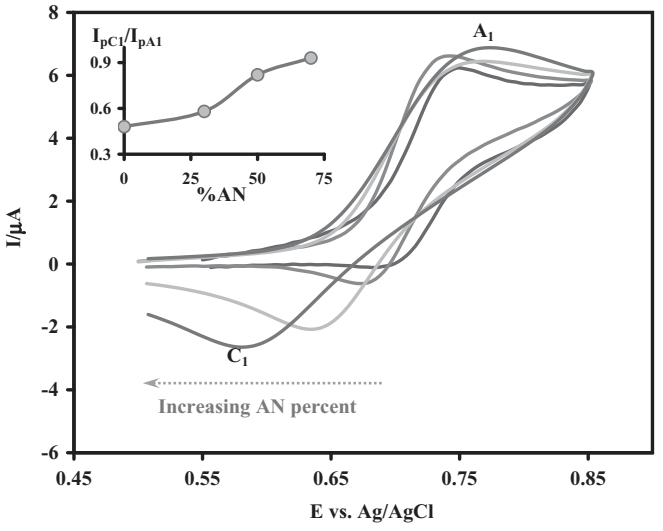


Figure 3. Cyclic voltammograms of 0.5 mM 4-phenylurazole (**1**) in 0.1 M HCl containing various percents of acetonitrile (AN) at a glassy carbon electrode. The percent of AN are 0, 30, 50 and 70% (v/v). Scan rate: 100 mVs^{-1} and $T = 25 \pm 1$°C.

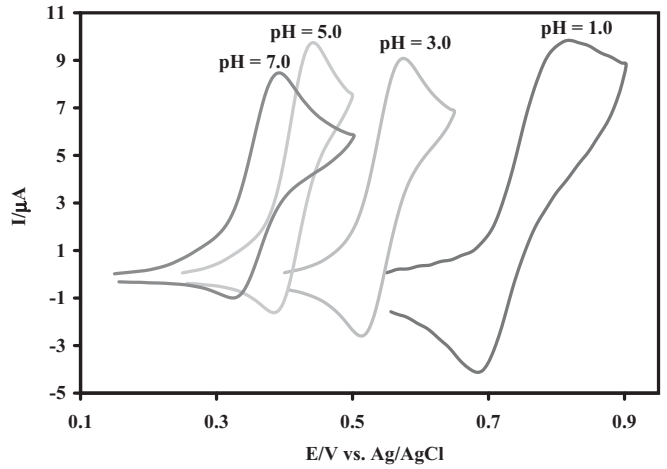


Figure 4. Cyclic voltammograms of 0.5 mM 4-phenylurazole (**1**) in buffer/AN (60/40, v/v) solutions with various pHs and the same ionic strength, at a glassy carbon electrode. Scan rate = 100 mV s^{-1} and $T = 25 \pm 1°C$.

Where m is the number of protons involved in the reaction and $E_{pA(pH=0)}$ is the anodic peak potential at pH = 0.0, R, T, and F have their usual meanings. An E_{pA}-pH diagram is constructed for oxidation of compound **1** by plotting the E_{pA} values as a function of pH (Fig. 5).

The E_{pA}–pH diagram comprise two linear segments with different equations and slopes around of pH = 5.3.

In pHs < 5.3:

$$E'_{pA} = 0.81 - 0.059\ pH$$

In pHs > 5.3:

$$E'_{pA} = 0.65 - 0.029\ pH$$

On the basis of the above mentioned slope, it can be concluded that the electrode surface reaction occurring at the pH > 5.3 is a two-electron, one-proton process involving the oxidation of "anionic form" **1** (**1An**$^-$) to the corresponding 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (**1ox**) (Scheme 1, Eq. 2). Whereas, the electrode surface reaction at pH < 5.3, corresponds to the two-electron, two-proton process (Scheme 1, Eq. 1). Also, the pK_a obtained in this work for acid/base equilibrium shown in Scheme 2 is: 5.3.

On the other hand, it is shown that the current of peak C_1 is strongly depended on the pH, so that with increasing pH the current of peak C_1 decreases. This peak disappears in pHs > 7.0. This data shows that by increasing pH, **1ox** is more unstable and disappears in the time scale of performed experiments. It is suggested that the observed instability corresponds to the nucleophilic addition of hydroxyl ion.

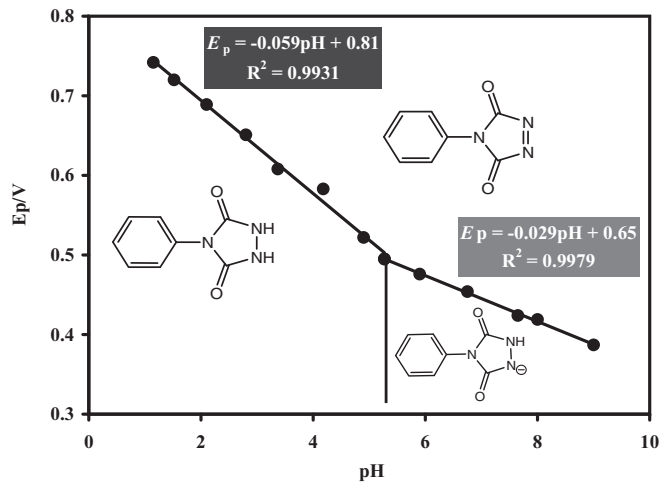
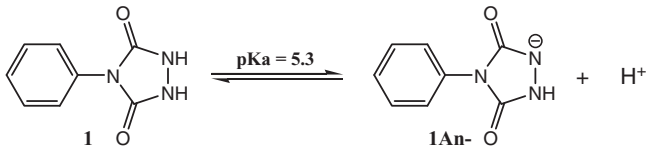


Figure 5. Variations of oxidation potential (E_{pA}) of 4-phenylurazole (**1**) as a function of pH, $T = 20 \pm 1°C$.



Scheme 2. Acid/base equilibrium of 4-phenylurazole (**1**).

The study of the effect of pH solution, solvent, 4-phenylurazole concentration and the potential scan rate on the cyclic voltammetric response indicates that the electrochemical oxidation of **1** is not a simple mechanism and a coupled chemical reaction participate in the oxidation pathway. Based on the 4-phenylurazole structure, some subsequent chemical reactions such as hydroxylation,[32,33] dimerization[34] and oxidative ring cleavage[26] are expected. Additionally, it cannot be considered dimerization of **1** and oxidized form of **1** (**1ox**) as the follow up chemical reaction. The data obtained from Fig. 2 shows the rate of the subsequent chemical reaction is independent on 4-phenylurazole concentration, so that with increase of concentration, the values of I_{pA1}/I_{pC1} remained constant. This observation is adapted with firs-order or pseudo-first order chemical reactions.

For more details, multi cyclic voltammograms repeated at the glassy carbon electrode don't show any alternation on the number of peaks (Fig. 6). These results reject hydroxylation of electrochemically generated 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (**1ox**) via Michael type reaction. Hydroxylation of 4-phenylurazole via Michael type reaction must show an *ECE* mechanism with appearing a new peak in multi-cyclic voltammetry.[32,33]

These voltammetry results accompanied by the previous published papers,[24,26,35] allow us to propose the following mechanism for the electrochemical oxidation of **1** (Scheme 3). According to the presented mechanism, it seems that electrochemically generated 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (**1ox**) is a reactive electrophile and nucleophilic addition of hydroxide ion (or water) to carbonyl group led to oxidative ring cleavage. Oxidative ring cleavage of **1** in the presence of hydroxyl ion (or water) is a pseudo-first order reaction. The above experimental results confirm the fact that the probability of dimerization reaction is very low. With increasing pH and decreasing AN percent, as the hydroxyl ion concentration increased the oxidative ring cleavage occurs faster, and the I_{pA1}/I_{pC1} ratio increased parallel to the increase of pH.

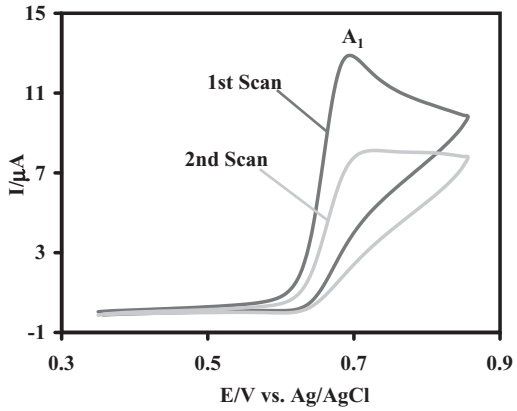
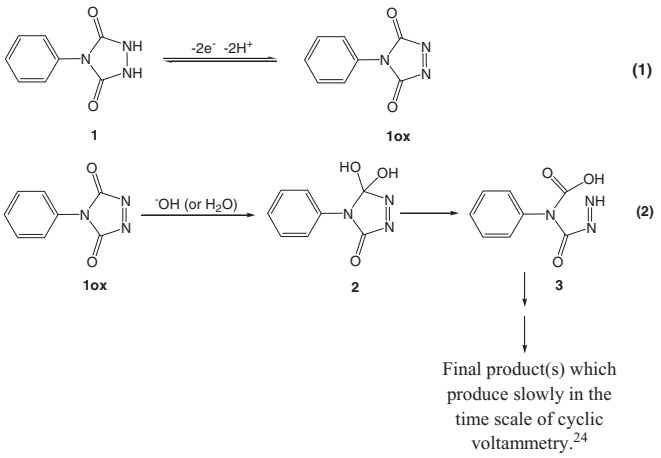


Figure 6. Multi-cyclic voltammogram of 1.0 mM 4-phenylurazole (**1**) in phosphate buffer (c = 0.2 M, pH = 2.0), at a glassy carbon electrode. Scan rate: 100 mV/s. $T = 25 \pm 1°C$.



Scheme 3. Oxidative ring cleavage mechanism of 4-phenylurazole (**1**).

Kinetic evaluation.— In the evaluating kinetic parameters, the Tafel plot was drawm (Fig. 7), derived from data of the rising part of the anodic branch of current-potential curves. This part of cyclic voltammogram, known as Tafel region, is affected by electron transfer kinetics between substrate (4-phenylurazole) and the electrode surface. In Tafel equation, $\log I = \log I_0 + \frac{(1-\alpha)nF}{2.30RT}\eta$, I_0 is exchange current, η is over voltage, and n, *R*, *T* and *F* have their usual meanings. The transfer coefficient, α, and exchange current density, J_0, evaluated from the slope and intercept of log *I*-η plot were found to be 0.52 and 3.7×10^{-3} μA cm^{-2} respectively, assuming two-electron transfer process.

Based on an *EC* mechanism under pseudo-first order conditions, the observed homogeneous rate constants (k_{obs}) of oxidative ring cleavage of 4-phenylurazole have been estimated in 0.1 M HCl containing different ratio of AN. The simulation was carried out assuming semiinfinite one-dimensional diffusion and planar electrode geometry. The experimental parameters entered for digital simulation consisted of the following: E_{start}, E_{switch}, E_{end}, $t = 25°C$ and analytical concentration of **1**. All these parameters were kept constant throughout the fitting of the digitally simulated voltammogram to the experimental data. The parameter k_{obs} was allowed to change through the fitting processes. The observed oxidative cleavage rate constants (k_{obs}) of **1ox** in various percents of water/acetonitrile are: 1.70 ± 0.126 (100%), 0.53 ± 0.068 (70/30%), 0.14 ± 0.011 (50/50%) and 0.04 ± 0.008 (30/70%) (Reported standard deviations were obtained for four independent scan rates). Also, the plot of k_{obs} of the ring cleavage of

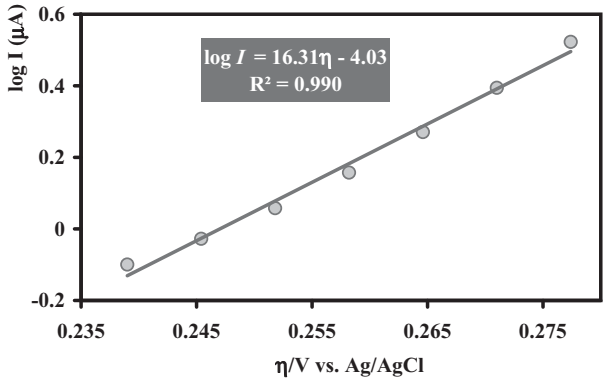


Figure 7. Tafel plot for the oxidation of 1.0 mM of 4-phenylurazole (**1**), Data obtained from the rising part of the anodic branch of cyclic voltammogram, with scan rate of 50 mV/s, in phosphate buffer ($c = 0.2$ M, pH = 2.0).

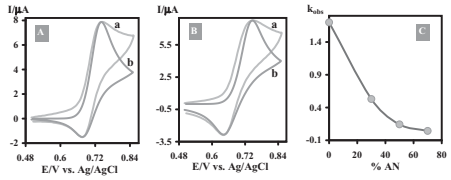


Figure 8. (A): experimental (a) and simulated (b) cyclic voltammograms of 0.5 mM 4-phenylurazole (**1**) in water/acetonitrile (50/50, v/v) solution containing 0.1 M HCl. Scan rate: 70 mV/s. (B) experimental (a) and simulated (b) cyclic voltammograms of 0.5 mM 4-phenylurazole (**1**) in water/acetonitrile (70/30, v/v) solution containing 0.1 M HCl, at a glassy carbon electrode. Scan rate: 60 mV/s. and (C) Variation of k_{obs} versus AN percent.

4-phenylurazole as a function of different percents of AN is shown in Fig. 8.

To study the effect of substituted group on the rate of oxidative ring cleavage, electrochemical oxidation of (4-(4-methoxyphenyl)-1,2,4-triazolidine-3,5-dione (**2**), 4-(4-chlorophenyl)-1,2,4-triazolidine-3,5-dione (**3**), 4-(3,4-dichlorophenyl)-1,2,4-triazolidine-3,5-dione (**4**) and 4-(4-nitrophenyl)-1,2,4-triazolidine-3,5-dione (**5**)) (Fig. 9) were also performed and k_{obs} of these urazole derivatives were calculated by digital simulation. The calculated values of the rate constant for oxidative ring cleavage have shown in Table I.

As shown in Table I, the magnitude of homogeneous rate constants depended on the nature of the substituted group on the phenyl ring. The presence of electron-donating groups such as methoxy causes a decrease in k_{obs}. As mentioned, 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (**1ox**) is very reactive as a result of the simultaneous presence of both carbonyl and azo moieties in the molecule. Therefore, 4-(4-methoxyphenyl)-4*H*-1,2,4-triazole-3,5-dione generated at the surface of electrode is more stable than **1ox**, by the presence of methoxy group as electron-donating group. In contrast, in the case of **3-5** the presence of chloro, dichloro and nitro groups with electron-withdrawing characters cause an increase in k_{obs}. Instability of oxidized forms of **3-5** becomes more critical as a result of the presence of electron-withdrawing groups on the phenyl ring. The first-order rate constants (k_{obs}) can be related with the Hammett ρ–σ parameters, where the Hammett equation is:

$$\log k_i = \log k_0 + \rho\sigma \qquad [2]$$

where k_i is the rate constant for substituted 4-phenylurazole, k_0 is the rate constant for 4-phenylurazole, σ is a constant characteristic of a given substituted group,[36] and ρ is the slope of the logk_i—σ graph. The Hammett plot is shown in Fig. 10.

Fig. 11, curve a, shows the cyclic voltammogram of 1.0 mM solution of 4-(4-nitrophenyl)-1,2,4-triazolidine-3,5-dione (**5**) in the aqueous acetate buffer solution ($c = 0.2$ M, pH 5.0) at a glassy carbon electrod in negative going scan. The voltammogram shows one cathodic peak (C_1) and anodic peak (A_2) at −0.55 and 0.20 V versus Ag/AgCl which correspond to the reduction of **5** to 4-(4-aminophenyl)-1,2,4-triazolidine-3,5-dione (**6**) (Scheme 4, Eq. 1) and oxidation of cathodically generated **6** to 4-(4-aminophenyl)-4*H*-1,2,4-triazole-3,5-dione

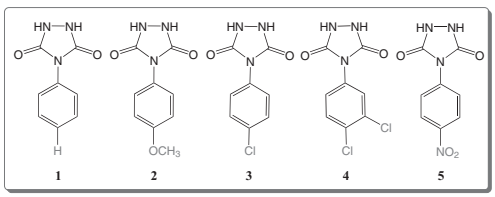


Figure 9. The structure of studied 4-phenylurazoles.

Table I. Calculated first-order rate constants (k_{obs}/s^{-1}) for oxidative ring cleavage of 4-phenylurazole derivatives in water/acetonitrile (60:40) solution containing 0.1 M HCl.

Phenylurazole derivatives[a]	1	2	3	4	5
k_{obs}/s^{-1}	$0.22 \pm 7.64\times10^{-3}$	$0.16 \pm 2.91\times10^{-3}$	0.43 ± 0.017	1.03 ± 0.026	2.56 ± 0.111

[a]Standard deviation of four independent simulations at various scan rates.

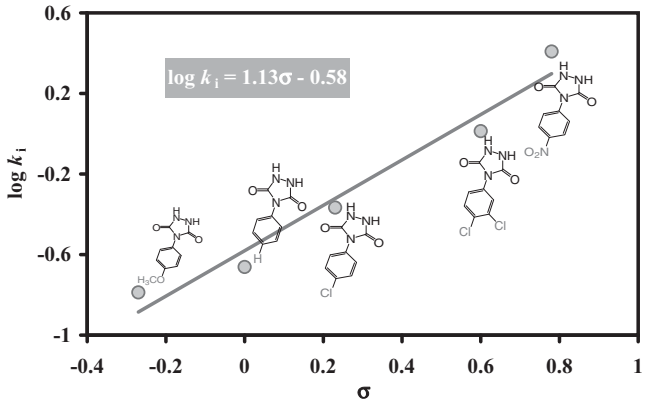


Figure 10. Hammett plot for studied 4-phenylurazoles.

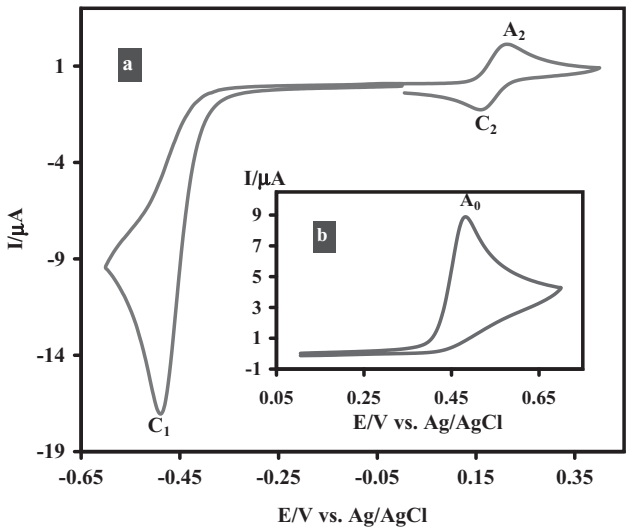
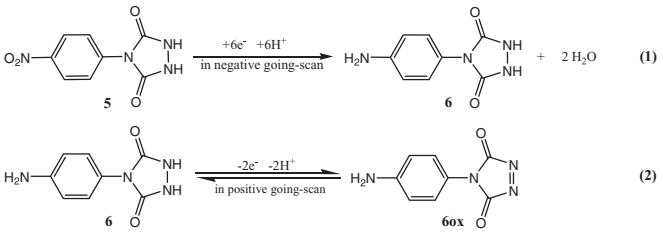


Figure 11. Cyclic voltammograms of 1 mM 4-(4-nitrophenyl)-1,2,4-triazolidine-3,5-dione (**5**) at a glassy carbon electrode, in acetate buffer solution ($c = 0.2$ M, pH 5.0). Scan rate: 50 mVs^{-1}; $T = 25 \pm 1°C$.



Scheme 4. Electrochemical reduction of **5** and oxidation of cathodically generated **6**.

(**6ox**) (Scheme 4, Eq. 2).[4] The cathodic peak C_2 is related to the reduction of **6ox** to **6**. Fig. 11, curve b, shows the cyclic voltammetry of **5** in positive going scan. The voltammogram shows one anodic peak (A_0) at 0.50 V vs. Ag/AgCl which correspond to the transformation of **5** to 4-(4-nitrophenyl)-4*H*-1,2,4-triazole-3,5-dione with an irreversible featur. In contrast to **5**, which shows an irreversible featur in low scan rate, the peak current ratio (I_{pC2}/I_{pA2}) of **6ox** is near unity and can be considered as slow oxidative cleavage rate constant and a criterion for the stability of **6ox** produced at the surface of electrode under the exprimental conditions. The stability of **6ox** is related to the presence of electron-donating group of $-NH_2$ on the phenyl ring.[4]

Chronoamperometry.— Chronoamperometry measurement of 4-phenylurazole (**1**) was done by setting the working electrode potential at 0.70 V and used for the measurement of the diffusion coefficient, *D*, of 4-phenylurazole (Fig. 12A).

The Shoup and Szabo theory model[37] has been used in order to determine diffusion coefficient of 4-phenylurazole. The fitting of

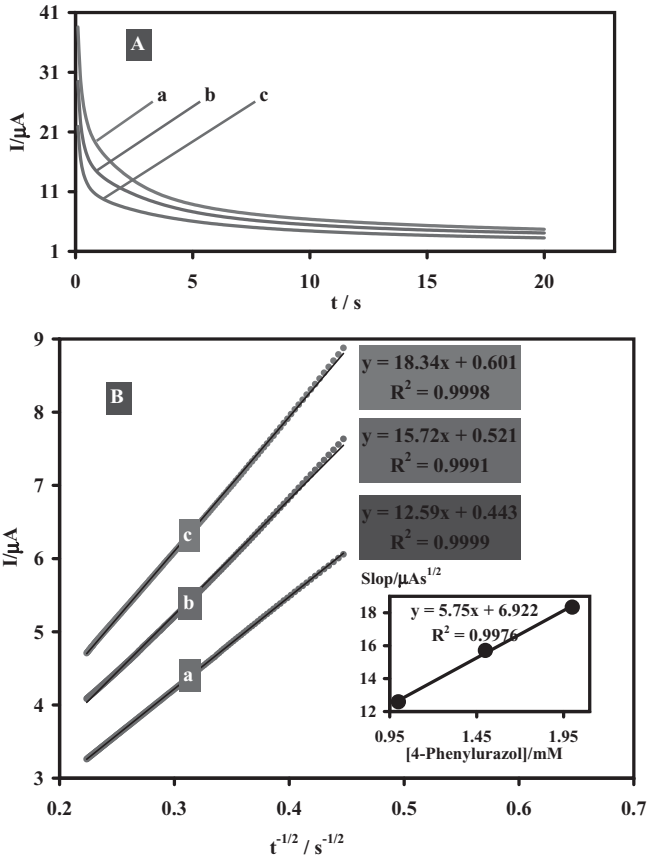


Figure 12. (A) Chronoamperometry responses at glassy carbon electrode in phosphate buffer solution (c = 0.2 M, pH 2) at potential step 0.7 V for different concentrations of 4-phenylurazole (**1**). Concentrations from a to c are: 1, 1.5 and 2 mM, respectively. (B) Plots of *I* versus $t^{-1/2}$ obtained for chronoamperograms shown in (A). Inset shows the plot of the slope of straight lines against the 4-phenylurazole concentrations.

Table II. Experimental thermodynamic parameters of 4-phenylurazole oxidation-reduction reaction in 20–45°C.

T (°C)	20	30	35	40	45
$E^{0'}$(V)[a]	0.797	0.792	0.790	0.787	0.784
lnK	63.13	60.66	59.53	58.35	57.22
$\Delta G(\frac{KJ}{molK})$	− 153.8	− 152.8	− 152.4	− 151.8	− 151.3

[a] Calculated by ploting of E_{pA}-pH at each temprature and by assuming that the $E^0 \approx E^{1/2} = E_{pA} - 28.5/n$ mV.

chronoamperogram in this method is expressed by Eq. 3 to 5.

$$\tau = \frac{4D_0 t}{a^2} \quad [3]$$

$$f_{(t)} = 0.7854 + 0.8862\tau^{-1/2} + 0.2146e^{-0.7823\tau^{-1/2}} \quad [4]$$

$$D_1 = \left| \frac{I}{4nFCaf_{(t)}} \right| \quad [5]$$

Where D is diffusion coefficient, t, time, a is the constant number of 0.09, C is concentration of 4-phenylurazole and n and F have their usual meanings. To determine diffusion coefficient, an assumption amount of D (D_0) is taken in Eq. 3 and τ, $f_{(t)}$ and D_1 is obtained from Eq. 3 to 5, respectively. Again, D_1 is taken in Eq. 3 and D_2 is resulted. This cyclic process is continued until the difference between two final D be negligible. A mean value of 1.60×10^{-5} cm^2/s was calculated for the diffusion coefficient. Also, the diffusion coefficient, D, is determined by Cottrell equation. For an electroactive material with a diffusion coefficient, D, the current for an electrochemical reaction is described by Cottrell equation.

$$I = \frac{nFAD^{1/2}C_b}{\pi^{1/2}t^{1/2}} \quad [6]$$

Where D and C_b are the diffusion coefficient and the bulk concentration, respectively. From the slop of I-$t^{-1/2}$, the diffusion coefficient can be obtained. Fig. 12B shows the experimental plot of I versus $t^{-1/2}$ along with the best fits for different concentrations of 4-phenylurazole. A mean value of 1.53×10^{-5} cm^{2}s^{-1} was calculated for the diffusion coefficient of I-$t^{-1/2}$ plots of different 4-phenylurazole concentrations. The determined D by this method is in agreement with calculated D from Shoup and Szabo theory model.

Calculation of thermodynamic parameters.— The effect of the temperature on the redox chemistry of **1** was studied in order to the calculation of some thermodynamic parameters, ΔH, ΔS and ΔG. The oxidation potential (E_{pA}) of a redox reaction is related to the temperature via the Eq. 1. As is clear, by increasing the temperature, E_{pA} shifts to the negative potentials. The thermodynamic parameters can be calculated according to the equations of 7–9.

$$\ln K = \frac{nFE^0}{RT} \quad [7]$$

$$\ln K = \left(\frac{-\Delta H}{RT}\right) + \left(\frac{\Delta S}{R}\right) \quad [8]$$

$$\Delta G^0 = -RT \ln K \quad [9]$$

Table II presents the equiliblium constants of 4-phenylurazole oxidation-reduction reaction (lnK) at 20–45°C. Fig. 13 shows the plot of lnK vs. $1/T$. By assuming that the enthalpy, ΔH, and entropy, ΔS, remain constant in the studied temprature range, these parameters evaluated from the slope and intercept, respectively, and were found to be −182.9 KJ/mol and −0.10 KJ/molK. The standard Gibbs free energy changes have been calculated using Eq. 9 and presented in Table II.

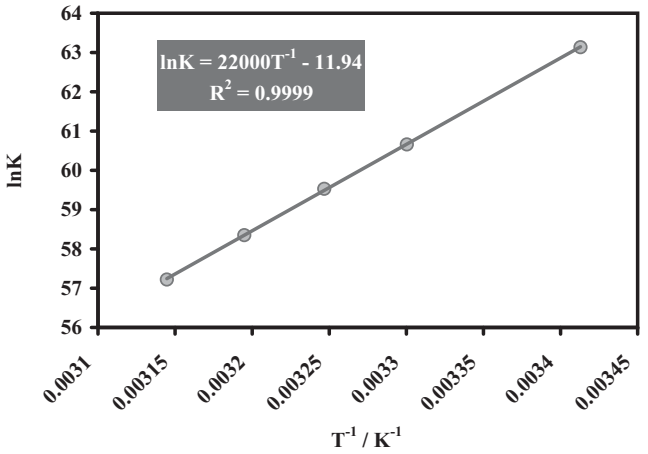


Figure 13. Variation of lnK versus $1/T$.

Conclusions

The results of this work show that 4-phenylurazole (**1**) is oxidized to 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (**1ox**). Our results indicate that in water, the electrochemically generated **1ox** is unstable as a result of simultaneous presence of both carbonyl and azo moieties in the molecule. Also, we studied the effect of 4-phenylurazole concentration, solvent and pH on the kinetic of ring cleavage of **1ox**. According to our results, the observed rate constant of ring cleavage of **1ox**, is depended on the hydroxyl ion concentration and *DN* of the solvent. On the other hand, the pH dependence of 4-phenylurazole was found to be −59 mV/pH, in the pH range from 1.0 to 5.3 and −29 mV/pH, in the pH range from 5.3 to 9.0, which are close to the anticipated Nerstian dependence of −59.0 and −29.5 mV/pH, respectively. The diffusion coefficient of **1** is calculated using chronoamperometric results. In the evaluating kinetic parameters the transfer coefficient, α, and exchange current density, J_0, calculated from the slope and intercept of log I-η plot, were found to be 0.52 and 3.7×10^{-3} μA cm^{-2}, respectively. In addition, we examined the kinetics of oxidative ring cleavage by digital simulation of cyclic voltammograms. Also, the effect of the temperature on the redox chemistry of **1** was studied in order to the calculation of some thermodynamic parameters, ΔH, ΔS and ΔG.

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