Electrochemical Behaviour of 3-Arylazo-1,2,4-triazole Compounds in Aqueous Buffered Solutions

Loutfy H. Madkour

Chemistry Department, Faculty of Science, Tanta University, 31527, Tanta, Egypt

A variety of electroanalytical methods, *e.g.* DC polarography, cyclic voltammetry and controlled potential coulometry have been employed upon 3-arylazo-1,2,4-triazole derivatives, AAT; substituents affect the reduction potentials but do not alter the reduction pattern.

In previous reports we have shown that aromatic azo and bisazo compounds are reduced at a DME along a single irreversible, diffusion-controlled wave, involving the transfer of two[1,3] or four electrons per molecule,[4,9,17] depending on the pH of the electrolysis medium and the type of substituent in the aromatic ring attached to the azo group. The importance of AAT compounds comes from their industrial[18] applications.

The investigated AAT compounds are shown below.
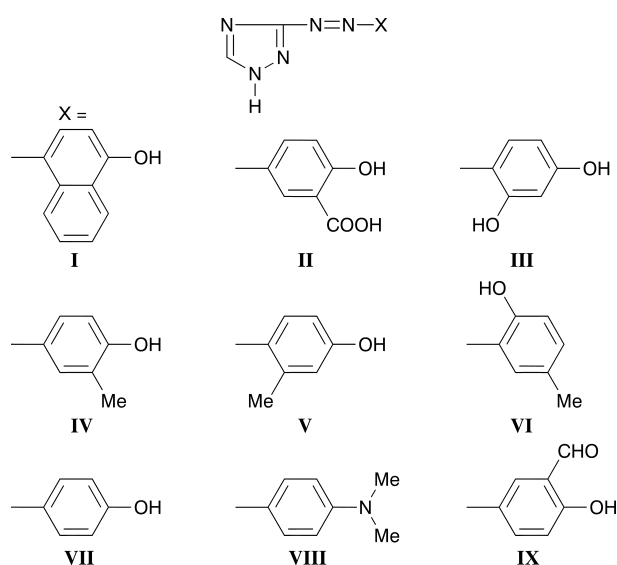
The polarograms consist of a single diffusion controlled irreversible wave ($\alpha < 1.0$). The results revealed that the rate-determining step should involve two electrons and one proton, which confirmed the reduction of the (N=N) centre to the corresponding hydrazo derivatives. The results are extended to the reduction of a molecule with two electrophores, namely an azo group and a carbonyl group.[21–23] These reduce independently along two consecutive, two-electron waves. The i_1 is pH-independent. The half-wave potential ($E_{1/2}$) for AAT compounds under investigation shifted to more negative values on increasing the pH, indicating that hydrogen ions are involved in the reduction process and that proton uptake precedes the electron transfer.[26] On plotting $E_{1/2}$ *versus* pH, broken lines consisting of one or two segments are observed. The inflections occur at pH $\approx$ 9.0, corresponding to the pK values of these AAT compounds calculated from spectroscopic and pH-meteric methods.

The hydrazo-products obtained using controlled potential electrolysis for AAT derivatives have been isolated and identified by spectroscopy (IR, UV, ^{1}H NMR) techniques.

The cyclic voltammograms of AAT compounds exhibit a single cathodic reduction peak at all pH values. The second peak for **1X** is owing to the reduction of the carbonyl group[21–23] in a separate step. The weak oxidation peaks
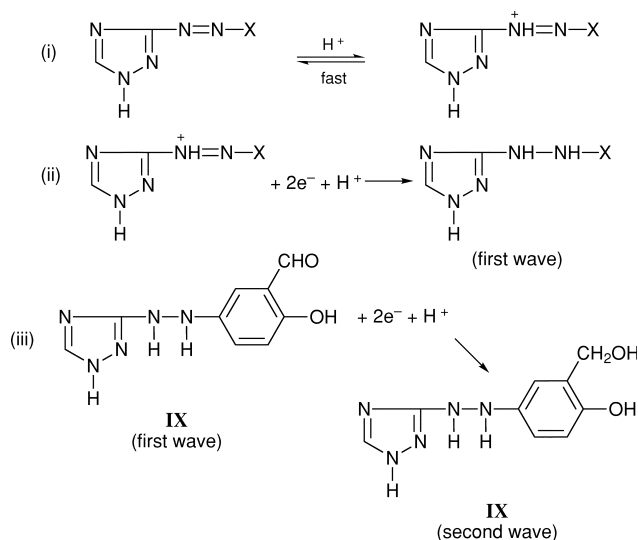
Scheme

observed in the cyclic voltammograms of some AAT derivatives may be attributed to an oxidation process of an anion free-radical originating from the one-electron reduction process[27] $-\overset{+}{N}H=N-+e \rightarrow NH-\dot{N}-$. This interpretation was investigated and supported on the basis of quantum mechanical calculations.[28] The irreversibility of the electrode process is confirmed by the absence of any peaks in the reverse scan as well, the shift of peak potential (E_p) to more negative values upon increasing the scan rate, and by the lower transfer coefficient (α) values.[30] The reduction process is controlled mainly by diffusion with some contribution from adsorption. This behaviour is supported from the values of slopes of log i_1/log h plots as well as the plots of peak current (i_p) as a function of the square root of the scan rate (v)$^{1/2}$ at different pH values. Reduction does not proceed to the amine stage since the aryl and triazole groups act as a barrier to electron transfer (Scheme).

Techniques used: Polarography, cyclic voltammetery, coulometry, IR, UV, ^{1}H NMR

References: 32

Table 1: DC-polarographic data for AAT compounds

Table 2: Data of cyclic voltammetery for AAT compounds

Scheme: 1

Fig. 1: Polarographic reduction waves of 0.25 mM **iv**

Fig. 2: Polarographic reduction waves of 0.25 mM **ix**

Fig. 3: $E_{1/2}$ *versus* pH for 3-arylazo-1,2,4-triazole compounds

Fig. 4: Cyclic voltammograms of 0.25 mM **i** at different scan rates in aqueous-buffered solution of pH 9.2

Fig. 5: Cyclic voltammograms of 0.25 mM **ix** at different scan rates in aqueous-buffered solution of pH 7.0

Fig. 6: Cyclic voltammograms of 0.25 mM **ix** at different scan rates in aqueous-buffered solution of pH 11.1

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