POLAROGRAPHIC BEHAVIOUR OF SOME ARYLAZOTHEOPHYLLINES

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The polarographic behaviour of a series of arylazotheophyllines was studied in aqueous alcoholic buffered media and in a DMF–0.1 M $LiClO_4$ solution. The redox study gave evidence that the azo group is electroactive in aqueous as well as non-aqueous media. A mechanism interpreting the electrode process is proposed and confirmed through the identification of the controlled potential electrolysis products, the use of a model compound and the application of Hammett's σ–E relationship. The physico-chemical characteristics of these compounds, viz. the diffusion coefficient, dissociation constant, ionization potential and electron affinity, are also included.

Azotheophylline derivatives have been reported to exhibit diverse pharmacological activities, including antispasmodic, diuretic, antiasthmatic, antihistaminic, and antimicrobial effects[1 – 4]. The interest of electrochemists in the electroreduction of heterocyclic azo compounds has increased recently[5 – 8]. In spite of the extensive work covering the electroreduction of the –N=N– azo moiety[9 – 11], no reference could be traced in the literature concerning the polarography of azotheophyllines. Thus, it appeared interesting to examine the polarographic behaviour of these compounds (*Ia* – *Ij*) in 50 vol.% aqueous alcoholic buffers covering a wide range of pH values and in DMF. The present study was undertaken with the following objectives: (i) To gain sufficient insight into the mechanism of the electrode process in order to be able to specify the optimum experimental conditions for the electrochemical reduction and oxidation of these compounds. (ii) To provide a simple electrochemical route for the synthesis of related organic molecules. (iii) To establish the predominant tautomeric structure in aqueous media.

Theophylline (*II*) has also been examined as a reference model compound under the same experimental conditions.

EXPERIMENTAL

Organic Synthesis

The 8-substituted phenylazotheophyllines (*Ia* – *Ij*) were prepared according to the following procedure[2,4]. The appropriate aromatic amine (0.002 mol) dissolved in 50% hydrochloric acid (10 ml) was cooled to 0 °C and then treated with a cold solution of sodium nitrite (0.14 g) in water (2 ml). The diazotized amine was added gradually to an ice-cold solution of theophylline (0.002 mol) in a mixture of ethanol (10 ml) and 10% NaOH solution (25 ml). The pH of the solution was then adjusted to 8 and the mixture was left in the ice box for 72 h. The reaction mixture was acidified with concentrated HCl. The separated product was filtered off, washed with water, dried, and recrystallized (Table I). The purity and structure were checked by measurements of m.p., NMR, IR, mass spectra and elemental analysis.

TABLE I
8-Arylazotheophyllines studied

Compound	Ar	M. p., °C Yield, %	Formula	Calculated/Found % C	 % H	 % N
Ia	C_6H_5	157[a]	$C_{13}H_{12}N_6O_2$	54.93	4.23	29.07
		57		54.84	4.22	28.99
Ib	*m*-$C_6H_4CH_3$	162[b]	$C_{14}H_{14}N_6O_2$	56.37	4.69	28.19
		59		56.33	4.71	28.16
Ic	*p*-$C_6H_4CH_3$	183[a]	$C_{14}H_{14}N_6O_2$	56.37	4.69	28.19
		55		56.40	4.66	28.12
Id	*m*-$C_6H_4OCH_3$	220[b]	$C_{14}H_{14}N_6O_3$	53.50	4.46	26.76
		52		53.43	4.41	26.75
Ie	*p*-$C_6H_4OCH_3$	239[b]	$C_{14}H_{14}N_6O_3$	53.50	4.46	26.76
		63		53.26	4.18	26.66
If	*m*-C_6H_4Cl	306[c]	$C_{13}H_{11}N_6O_2Cl$	48.97	3.45	26.37
		61		48.84	3.41	26.22
Ig	*p*-C_6H_4Cl	222[c]	$C_{13}H_{11}N_6O_2Cl$	48.97	3.45	26.37
		59		48.91	3.38	26.41
Ih	*m*-C_6H_4Br	331[c]	$C_{13}H_{11}N_6O_2Br$	42.98	3.30	23.43
		65		42.87	3.27	23.18
Ii	*p*-C_6H_4Br	335[c]	$C_{13}H_{11}N_6O_2Br$	42.98	3.30	23.43
		68		42.73	3.35	23.48
Ij	*p*-$C_6H_4NO_2$	341[d]	$C_{13}H_{11}N_7O_4$	47.41	3.34	28.79
		60		47.37	3.36	28.66

Crystallized from: [a] acetic acid; [b] benzene–petroleum ether 40 – 60 °C; [c] acetic acid–water; [d] ethanol.

Polarographic Investigation

Apparatus and measurements. Polarographic curves were recorded with a Sargent Welch polarograph Model XVI. A cell of our own design with a separated saturated calomel electrode (SCE) was used[12]. The capillary had the following characteristics in open circuit: $t = 4.35$ s, $m = 1.98$ mg s^{-1} for $h = 51$ cm. An ASA 100 Tacussel potentiostat was used for controlled potential electrolysis (CPE). The amount of electricity was measured with an electronic Tacussel integrator type IG3A.

All experiments were carried out at 25 ± 0.1 °C. The half-wave potentials ($E_{1/2}$) were measured graphically and expressed vs SCE with an accuracy of ±0.005 V.

Procedure. The depolarizer concentration was 5 . 10^{-4} mol l^{-1} in DMF–0.1 M $LiClO_4$ solution and ethanol–Thiel buffer mixtures 1 : 1 (vol.). Thiel buffer is composed of boric acid, sodium sulfate, succinic acid and borax solutions[12]. Concentrated solution of NaOH was used to raise the pH of the medium to pH > 12, whereas, few drops of concentrated HCl were added to decrease the pH to below 3.1. The pH measurements were performed using a Radiometer M28b pH-meter equipped with glass–calomel electrodes. Prior to each run, pure nitrogen gas was bubbled through the polarographic cell. At pH < 8.5, the polarogram is distorted by a polarographic maximum which can be eliminated by the addition of 0.0013% Triton X-100.

Controlled Potential Electrolysis and Identification of the Resulting Products

CPE was carried out in 40 ml of a mixture of 50 vol.% ethanolic buffer and 5 . 10^{-4} mol l^{-1} of substance *Ia* as representative for the series studied. The potential was controlled at the limiting current plateau of the cathodic waves as taken from their polarograms under the same experimental conditions. The experiment was carried out twice at controlled potentials of −0.5 V and −1.0 V for waves *A* and *B*, respectively.

Electrolysis at −0.5 V (wave A). The progress of electrolysis was followed by recording the decrease in current with time. The number of electrons spent per molecule of substrate, which was calculated from the *i–t* curves following the procedure outlined by Lingane[13], was found to be 4. After disconnecting the electrolysis cell from the circuit, 1 ml of the resulting solution was withdrawn and the presence of aniline was revealed by a standard spot test[14]. The remaining reaction mixture was partly evaporated on a water-bath to 1/3 of its original volume and the organic substances were extracted with dry ether. The ether layer was then removed and evaporated in vacuo. The remaining faint yellow residue was identified as 8-aminotheophylline (*IV*) by elemental analysis, m.p., NMR and IR spectra.

Electrolysis at −1.0 V (wave B). When the polarographic trace of compound (*Ia*) disappeared completely, the solution was treated as above. The number of electrons per molecule consumed along wave *B* was found to be 2. Ammonia was detected with Nessler's reagent[15]. The insoluble moiety was isolated, found identical with the model compound *II*, and identified as theophylline (*V*).

It is noteworthy that the IR spectra of both *IV* and *V* show one band at 1 575 – 1 535 cm^{-1} corresponding to the azo group.

Determination of the Acid Dissociation Constants pK_a

The pK_a value of the compounds studied were evaluated spectrophotometrically[16] in 50 vol.% ethanolic buffer solutions at an ionic strength of 0.1 mol l^{-1} and at 25 ± 0.1 °C. The electronic absorption spectra were measured on a Pye–Unicam SP 8000 instrument. The pK_a value was calculated using the equation

$$\mathrm{pH} = \mathrm{p}K_a + \log (A - A_{\min})/(A_{\max} - A).$$

The intercept of the straight line of the pH vs $\log(A - A_{min})/(A_{max} - A)$ plot with the pH axis at $\log(A - A_{min})/(A_{max} - A) = 0$ directly gave the pK_a value.

RESULTS AND DISCUSSION

Polarographic Behaviour of Compounds Ia – Ij

Polarograms of 5 . 10^{-4} mol l^{-1} of *Ia* – *Ij* in 50 vol.% ethanolic Thiel buffers are exemplified by those of *Ia* shown in Fig. 1. In the range of pH 2 – 8, the polarograms exhibit two waves *A* and *B* with height ratio 2 : 1. At pH > 8, the height of wave *B* starts to decrease. In addition to waves *A* and *B*, compound *Ij* showed an additional irreversible diffusion-controlled wave *C* at a more negative potential. Comparison of polarograms of *Ij* with those of *Ia* – *Ij* suggests that wave *C* is due to the p-NO_2 group. Also, a wave-height ratio comparison indicates that wave *C* is a 4-electron step and the $E_{1/2}$–pH plot appears compatible with that reported for the reduction of aromatic nitro groups to hydroxylamine derivatives. At pH > 10, another ill-defined wave *D* appears with a limiting current corresponding to 2 electrons and with a pH dependent $E_{1/2}$ value, which is ascribed to a further reduction of the hydroxylamine to amine[17].

$$-NO_2 + 4\,e + 4\,H^+ \xrightarrow{E_1^c} -NHOH + H_2O$$

$$-NHOH + 2\,e + 2\,H^+ \xrightarrow{E_2^d} -NH_2 + H_2O$$

Nature of Waves A and B

The limiting current i_l of waves *A* and *B* at different heights of mercury column is found to satisfy the relationship $i_l = Kh^x$ with x varying within the range of 0.45 – 0.56. The

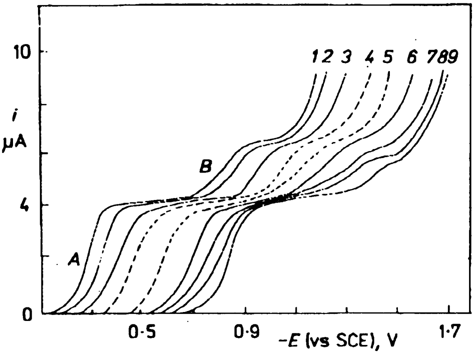


FIG. 1
Polarograms of 5 . 10^{-4} mol l^{-1} *Ia* in 50 vol.% ethanol–Thiel buffer solutions at pH: *1* 2.1, *2* 3.1, *3* 4.3, *4* 5.8, *5* 7.1, *6* 8.3, *7* 9.9, *8* 11.1, *9* 12.1

linear relationship between i_l and C up to 1.34 m mol l^{-1} passing through the origin may provide additional evidence that the reduction process is diffusion controlled.

The cyclic voltammograms, using a hanging mercury drop, of the compounds under investigation at different sweep rates (20 – 500 mV s^{-1}) display three peaks in the cathodic scan (Fig. 2) but do not exhibit any anodic peaks in the reverse scan. This indicates an irreversible nature of the reduction waves. The shift of the peak potential E_p to more negative values by increasing the sweep rate confirms such irreversibility.

The kinetic parameters of the electrode reduction processes can also be estimated from the correlation of E with log $(i/i_l - i)$ at different pH values. The results (Table II) indicate that the two waves proceed irreversibly, the irreversibility being higher as the pH is increased. This situation is supported by the values of the transfer coefficient, the lower values of the electron rate constant (K_e^0) and the higher values of the activation free energy (ΔG^*), as calculated by applying the various approaches to the analysis of irreversible waves[18 – 21]. The diffusion coefficient (D) of the depolarizer was determined experimentally by applying the Stokes–Einstein equation[22].

The effect of pH on the half-wave potentials of waves A and B is illustrated in Fig. 3. The $E_{1/2}$ values of waves A and B are pH-dependent. For wave A, the shift of $E^a_{1/2}$ with increasing pH is linear up to pH 10, above which the $E_{1/2}$–pH dependence is much less pronounced. The shift of $E^a_{1/2}$ by an average 70 mV/pH over the range of pH 2 – 10 along with the independency of the wave height of pH is a direct indication that the molecule is protonated prior to its electrochemical reduction[6,10]. This is confirmed by applying the equation $dE_{1/2}/dpH = (-2.3RT/\alpha nF)Z_{H^+}$ which gives the number of hydro-

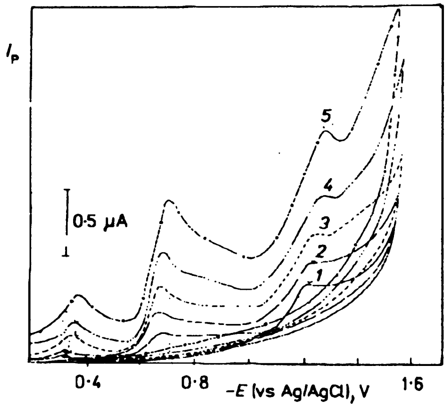


FIG. 2
Cyclic voltammograms of *Ia* at pH 3.1. Sweep rate (mV s^{-1}): *1* 20, *2* 50, *3* 100, *4* 400, *5* 500

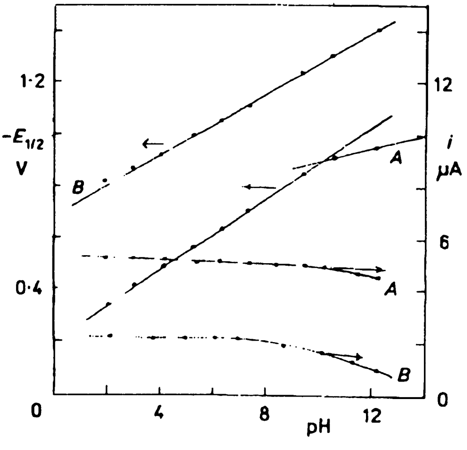


FIG. 3
Correlation of $E_{1/2}$ and i_l with pH

TABLE II
Polarographic data of some arylazotheophyllines

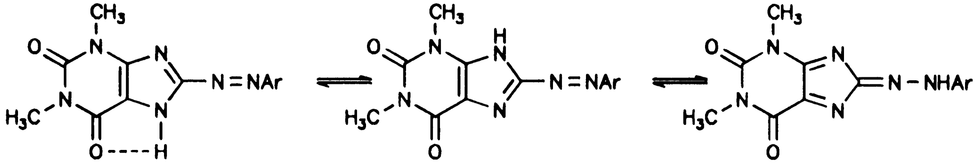
Compound	pH	Wave	$-E_{1/2}$	$D \,.\, 10^6$ $cm^2\,s^{-1}$	s^a	αn	$\Delta E_{1/2}/\Delta pH$	Z_{H^+}	$K c°$ $cm\,s^{-1}$	$\Delta G^* \,.\, 10^{-2}$ $kJ\,mol^{-1}$
Ia	2.,1	*A*	0.33	5.83	16.0	0.94	0.071	1	$3.6 \,.\, 10^{-8}$	3.5
		B	0.81		15.8	0.93	0.068	1	$1.5 \,.\, 10^{-11}$	4.6
	5.8	*A*	0.61		14.3	0.84		1	$6.4 \,.\, 10^{-10}$	3.7
		B	1.02		15.4	0.91		1	$3.3 \,.\, 10^{-13}$	4.9
	11.1	*A*	0.94		12.2	0.72	0.034	0.42	$1.9 \,.\, 10^{-12}$	4.4
Ib	2.1	*A*	0.36	6.39	15.6	0.92	0.069	1	$3.1 \,.\, 10^{-8}$	3.6
		B	0.84		15.3	0.90	0.068	1	$8.8 \,.\, 10^{-10}$	4.3
	5.8	*A*	0.66		14.0	0.83		1	$5.1 \,.\, 10^{-11}$	4.6
		B	1.05		15.0	0.89		1	$6.2 \,.\, 10^{-13}$	5.0
	11.1	*A*	0.98		11.6	0.69	0.031	0.36	$6.6 \,.\, 10^{-12}$	4.3
Ic	2.1	*A*	0.34	6.31	15.6	0.92	0.070	1	$2.7 \,.\, 10^{-8}$	4.4
		B	0.82		15.0	0.89	0.067	1	$3.3 \,.\, 10^{-11}$	4.6
	5.8	*A*	0.63		14.1	0.83		1	$6.1 \,.\, 10^{-10}$	3.8
		B	1.03		14.9	0.88		1	$4.8 \,.\, 10^{-13}$	4.9
	11.1	*A*	0.96		12.1	0.71	0.032	0.39	$2.2 \,.\, 10^{-12}$	4.4
Ie	2.1	*A*	0.35	6.40	15.3	0.90	0.071	1	$4.3 \,.\, 10^{-8}$	3.5
		B	0.81		14.9	0.88	0.069	1	$3.3 \,.\, 10^{-11}$	4.6
	5.8	*A*	0.67		14.9	0.88		1	$5.7 \,.\, 10^{-10}$	3.8
		B	1.03		13.2	0.78		1	$6.3 \,.\, 10^{-13}$	4.9
	11.1	*A*	0.96		10.8	0.64	0.033	0.36	$8.3 \,.\, 10^{-11}$	4.4
Ig	2.1	*A*	0.28	5.88	15.4	0.91	0.070	1	$8.6 \,.\, 10^{-7}$	3.5
		B	0.76		14.9	0.88	0.068	1	$2.1 \,.\, 10^{-11}$	3.7
	5.8	*A*	0.55		14.9	0.88		1	$4.2 \,.\, 10^{-10}$	3.8
		B	0.95		13.5	0.80		1	$1.8 \,.\, 10^{-13}$	4.9
	11.1	*A*	0.88		11.1	0.65	0.032	0.35	$2.1 \,.\, 10^{-12}$	4.4
Ii	2.1	*A*	0.26	5.86	15.4	0.91	0.070	1	$4.5 \,.\, 10^{-8}$	3.6
		B	0.75		15.1	0.89	0.068	1	$9.3 \,.\, 10^{-10}$	4.1
	5.8	*A*	0.52		14.7	0.87		1	$2.2 \,.\, 10^{-10}$	3.8
		B	0.91		14.3	0.85		1	$1.5 \,.\, 10^{-13}$	4.9
	11.1	*A*	0.84		12.3	0.72	0.033	0.40	$2.1 \,.\, 10^{-12}$	4.4
Ij	2.1	*A*	0.18	5.59	15.9	0.94	0.070	1	$3.3 \,.\, 10^{-8}$	3.5
		B	0.85		15.6	0.92	0.069	1	$1.4 \,.\, 10^{-11}$	4.6
	5.8	*A*	0.43		14.4	0.85		1	$5.8 \,.\, 10^{-10}$	3.8
		B	1.07		15.0	0.77		1	$3.1 \,.\, 10^{-13}$	4.0
	11.1	*A*	0.78		12.1	0.71	0.031	0.37	$1.1 \,.\, 10^{-12}$	4.3

[a] Slope of logarithmic analysis.

gen ions (Z_{H^+}) per molecule[23]. At pH > 10, the shift of $E^{a}_{1/2}$ is 32 mV/pH; this can be taken as an indication that at these higher pH values both the protonated and unprotonated species are reduced at compatible potentials and that the unprotonated form predominates.

The Electrode Mechanism

It is well known that the cyclic C=O, C=C, C=N as well as the exocyclic N=N groups are the possible reduction sites in arylazotheophyllines *Ia* – *Ij*. It was of interest to determine which part of the molecule is the electroactive site. The polarograms of the model compound *II* were measured under the same experimental conditions as that of *Ia*. No wave was observed which indicates that under the conditions applied, the heterocyclic ring is electroinactive and the center N=N is the only electroactive site. On the other hand, the compounds under study can take one of the three potentially tautomeric structures *I*α – *I*γ, i.e., the active center can exist in the azo or in the hydrazono form.



Iα *Iβ* *Iγ*

It has been demonstrated previously that in the case of an irreversible 4-electron step, a comparison based on $E_{1/2}$ measurements to differentiate between azo and hydrazono structures can be misleading[24,25]. Also, the use of UV and IR data alone fails to give complete information on the structure[26,27]. Moreover, identification of the CPE products would give no conclusive information since in this case both azo and hydrazono compounds are reduced to the corresponding amines[28,29]. Thus, investigation of the behaviour of nitro derivatives under the same conditions seems to be the most appropriate ways, since it has been established and well documented that the nitro group is reduced before the hydrazono (–C=N–NH) linkage and after the azo (–N=N–) moiety[30 - 32].

Based on the isolated products from CPE as well as the polarographic data obtained, the following mechanism can be suggested for the electrochemical reduction of compounds *Ia* – *Ij* at the DME.

Wave A. The behaviour of this wave is consistent with the reported behaviour of compounds containing the azo group but differs markedly from that of compounds containing the hydrazono linkage. This may be confirmed by the appearance of the wave corresponding to the nitro moiety in compound *Ij* after wave *A*. Also, the main products of electrolysis (CPE at this wave) gave 8-aminotheophylline (*IV*) and aniline; this is an evidence in support of the hypothesis that the –N=N– group is the site attacked. Thus, one can assume that structures *Iα* and *Iβ* are the most probable in 50 vol.% ethanolic aqueous media. Moreover, structure *Iα* can be further stabilized through hydrogen bonding between carbonyl group (in position 6) and the H attached to N (in position 7).

$$\underset{I}{\text{Y–N=N–Ar}} + H^+ \rightleftharpoons \underset{II}{[\text{Y–N=N–Ar}]H^+}$$

$$II + 2\,e + H^+ \xrightarrow{E_1^a} \underset{III}{\text{Y–NH–NH–Ar}}$$

$$III + 2\,e + 2\,H^+ \xrightarrow{E_2^a} \underset{IV}{\text{Y–NH}_2} + \text{ArNH}_2$$

$$E_1^a = E_2^a = E_{1/2}^a$$

Y = Theophylline moiety

The appearance of a single wave *A* seems to be related to the fact that the energies E_1^a and E_2^a of the individual steps are very close to one another. Thus, only one amalgamated 4-electron step is displayed. The fact that this wave predominates across the whole pH range suggests that these molecules are highly basic in nature which is borne out by their pK_a values (cf. Table III).

Wave B. This wave corresponds to a 2-electron step and represents the reduction of the protonated form *IV* via the reductive splitting of $C–NH_3^+$. A similar reductive splitting has been reported before by Zuman for α-amino ketones[33]. The isolation and identification of theophylline *V* as well as the quantitative determination of the ammonia produced corroborated the mechanism. The decrease in the height of wave *B* with increasing pH gives evidence that the protonated form *IV* is the electroactive species. Thus, as the pH increases, the protonation reaction is no longer sufficient to take place.

$$IV + H^+ \longrightarrow \text{Y–NH}_3^+ \xrightarrow[E_{1/2}^b]{2\,e\, +\, H^+} \underset{V}{\text{Y}} + \text{NH}_3$$

The most reliable $E^{a}_{1/2}$ data at selected pH values have been correlated with the various Hammett's constants[34]. Statistical treatment of the data was carried out using Jaffe calculations[35]. Representative $E_{1/2}$–σ plots possess a reasonable linearity, the specific reaction constant (ρ) values varying between 0.183 and 0.296 for the σ and σ^0 constants. These values are consistent with those reported for arylazo but not for hydrazones[36]. The positive value of ρ indicates a nucleophilic mechanism (i.e. electron uptake as the potential determining step) and the substituents can affect the reaction center by their inductive effect but not through the mesomeric effect. It should be recalled that the $E_{1/2}$–σ plots (Fig. 4) include points corresponding to the p-NO_2 derivative calculated by adopting σ(p-NO_2). These points fit properly in the linear relationship. If, however, the σ(p-NHOH) or σ(p-NH_2) constants are used, con-

TABLE III
Physico-chemical characteristics of some arylazotheophyllines

Compound	pK_a	$-E^{R}_{1/2}$, V	$-E^{OX}_{1/2}$, V	$\Delta E_{1/2}$, V	EA, eV	IP, eV
Ia	10.9	0.72	0.21	0.51	1.8	5.5
Ib	11.1	0.78	0.27	0.51	1.7	5.4
Ic	11.0	0.76	0.23	0.53	1.7	5.5
Id	11.3	0.74	0.22	0.52	1.8	5.5
Ie	11.3	0.75	0.24	0.51	1.7	5.5
If	10.4	0.70	0.18	0.52	1.8	5.6
Ig	10.3	0.67	0.13	0.54	1.8	5.6
Ih	10.2	0.69	0.19	0.50	1.8	5.5
Ii	10.2	0.66	0.12	0.54	1.8	5.6

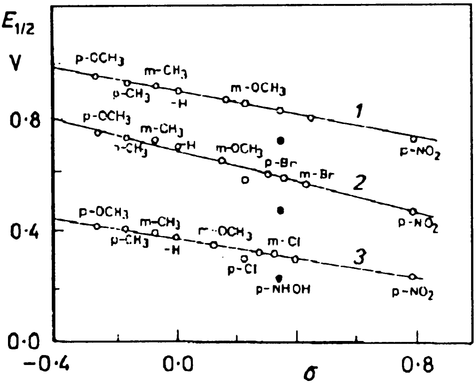
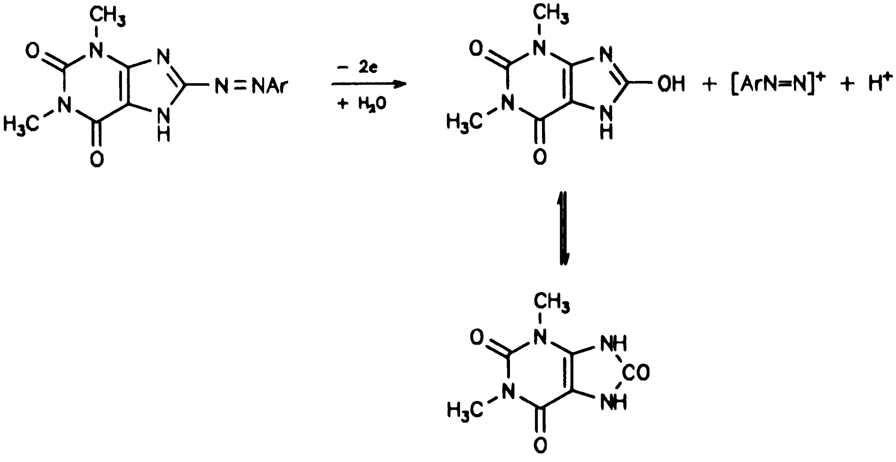


FIG. 4
Correlation between $E_{1/2}$ and σ at pH: *1* 11.1, *2* 7.1, *3* 3.1

siderable deviations are obtained. This provides another evidence that these compounds are in the azo form (not hydrazono) as the –N=N– moiety is reduced prior to the NO_2 group.

Finally, the cathodic and anodic behaviour of compounds (*Ia* – *Ij*) was examined in DMF containing 0.1 M $LiClO_4$ as the supporting electrolyte. The results reveal that the reduction behaviour of these compounds in DMF approaches that in aqueous alcoholic buffer solutions. However, the anodic oxidation of these compounds gives rise to a single irreversible diffusion-controlled wave. Through the inspection of the height ratios and with the aid of the Ilkovič equation, the anodic wave was found to correspond to a 2-electron step, i.e., to the oxidation of *Ia* to 1,3-dimethyluric acid.

The substituent effects on the electrochemical oxidation of *Ia* – *Ij* are apparent from the shift of $E^{OX}_{1/2}$ (Table III). Electron withdrawing substituents shift $E^{OX}_{1/2}$ to more positive potentials, whereas electron donating substituents increase the electron density at the azo group thus facilitating the oxidation process. This can be regarded as evidence that the oxidation takes place at the azo moiety.



1,3-dimethyluric acid

The half-wave reduction $E^{R}_{1/2}$ and oxidation $E^{OX}_{1/2}$ potentials are taken as measures of the electron affinity (*EA*) and ionization potential (*IP*) according to the following equations[12,37 – 39].

$$EA = -E^{R}_{1/2} + 2.5 \pm 0.3$$

$$IP = 1.5\,E^{OX}_{1/2} + 5.8$$

The obtained values of $E^{R}_{1/2}$, $E^{OX}_{1/2}$, *EA* and *IP* are summarized in Table III.

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