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AZO - HYDRAZO TAUTOMERISM: FURTHER EVIDENCE BASED ON POLAROGRAPHIC REDUCTION AND ACIDITY FUNCTION OF SOME HETEROCYCLIC COMPOUNDS CONTAINING OXIMINO - GROUP

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ABSTRACT

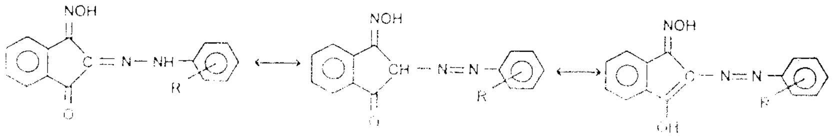
Potentiometric pK_a and polarographic behaviour of 1, 3–indandione–monoxime and four of its substituted derivatives were investigated in buffer solution of pH ~ 2–12. The results showed that the compounds are in the azo–form, where its reduction wave precedes that of the oxime. A mechanism for the electrodic processes was proposed. Half–wave potentials showed fair correlation with Hammett's σ constants while pKa is practically independent.

INTRODUCTION

The conflict of azo–hydrazo tautomerism in aqueous media have been delt polarographically. An uptake of 2e in a reversible wave, by compounds capable of existing in both tautomeric forms is taken as an azo form reducing according to the following reaction[1–6]

$$R_1 - N = N - R_2 + 2H^+ + 2e \rightleftarrows R_1 - NH - NH - R_2$$

If the reduction of the molecule under investigation consumes 4e, one should be cautious since differentiation between azo/hydrazo tautomeric system on the basis of $E_{1/2}$ can be misleading[7–12]. In such cases the behaviour of the nitro substituent in any location of the molecule have been reported to discriminate between both tautomeric forms. The importance of the nitro derivative lies in the fact that literature survey of an azo compound containing a nitro substituent the $-N=N-$ group is reduced before the nitro[3,7,8] group, while if a hydrazone form, $>C=N-NH-$ prevails the opposite reduction sequence occurs[9–11]. In a previous work we aimed to approach this point through studying the effect of polarographically active group (namely oxime)[12]. The results showed that in case of acyclic compound the oxime group is reduced first followed by a hydrazone (and not azo) group. Going in this direction it seemed to us worthwhile to investigate the role of the oxime group in conjunction with an azo / hydrazo group in a cyclic compound (I)



I

R : a = H
b = p - CH_3
c = p - O CH_3
d = p - Cl
e = m - NO_2

The role of substituent, particularly the nitro derivative on the ease of reduction and acid–base equilibrium was also examined to evaluate the fidelity of applying LFER to the compounds under consideration.

EXPERIMENTAL

Organic Syntheses

The parent compound I_a was prepared following procedures described by Gudriniece and Vanagas[13] by coupling diazotized aniline with 1,3 –indandione whereby 2–phenylazo 1,3 –indandione is formed which on recrystallization from alcohol separates in fine lustrous deep brown crystals, m.p. 192°. The later is then refluxed with hydroxylamine hydrochloride in alcohol for 2 hr. After cooling I_a separates, filtered recrystallized from alcohol whereby I_a (2–phenyl azo–1,3 –indandione monoxime) is obtained, m.p. 264–5°C. Following similar procedures compounds $I_{b,e}$ were obtained by coupling the respective diazotized substituted aniline with 1,3 –indandione. Purity credit of the products were checked by microelemental analyses and TLC of the recrystallized products.

Polarographic Investigation

Apparatus

Polarograms were recorded with a pen type recording polarograph (E 506 Metrohm, Switzerland). The capillary possessed the following characteristics in H_2O open circuit: $t = 4.6s\ drop^{-1}$, $m = 1.43\ mg\ s^{-1}$ for $h = 40$ cm.

Solution

Stock solution (10^{-3} mol L^{-1}) were prepared by dissolving an accurately weighed quantity of material in the appropriate volume of absolute ethanol. Due to the limited solubility of the m–NO_2 derivative (I_e), the material was dissolved first in 5 ml of DMF. Britton–Robinson modified universal buffers[15] were used as supporting electrolyte.

Measurement

All experiments were carried out at 25 ± 2°C. The $E_{1/2}$ were measured graphically and expressed vs. SCE with an accuracy of ± 5 mV. The solution pH was measured directly after each polarographic run using glass electrode. The latter was previously calibrated in ethanolic solutions following the procedures outlined by van Uitert and Hass[16].

Procedure

Ethanol (6 ml) and the appropriate buffer solution (12 ml) were introduced in the polarographic cell and deaereted with a stream of purified nitrogen for 12 min. The calculated amount of stock solution (2 ml) was then introduced into the cell so that the final concentration of depolarizer was 10^{-2} M in 20 cm^3 of 40 % (V / V) ethanolic buffer.

Determination of the Number of Electrons (n)

Controlled potential electrolysis (cpe) was carried out on 200 ml of 10^{-2} mol L^{-1} of I_a at pH 4.2 which is 40 % (V / V) ethanolic buffer. The electrolysis cell was 250 ml conical flask with a working area of — 50 cm^2 in which the reference and auxiliary electrodes, and the gas inlet were aaded through a cork. The potential was controlled at –0.60 V vs. SCE (i.e. on the limiting current plateu of wave a). Progress of electrolysis was followed by recording the decrease in current with time and the number of electrons involved in the electrode process was computed from i–t curves following the method outlined by Lingane[17]. For wave a the number of electrons was calculated and found to be 3.87 ($n = 4$). Comparison of the wave–heights of waves a and b showed that wave (b) is reduced in 4e wave. After complete electtrolysis the cell was disconnected and aniline was detected in the electtrolysed solution using the anthranilic acid spot test[18].

Determination of Apparent Dissociation Constant by Potentiometry

A freshly prepared stock solution of 10^{-3} mol L^{-1} (I_{a-e}) in 20 ml ethanol is placed in 100 ml beaker, diluted to 40 ml with distilled water so that the final concentration of the studied compound is 5×10^{-4} mol L^{-1} in 50 % V / V ethanolic aqueous solution. The latter was then titrated against 10^{-2} mol L^{-1} carbonate free–sodium hydroxide solution with continuous stirring. The constant pH after each base addition was read on a digital pH meter (HANNA HI 9017 microprocessor) accurate to ± 0.01 pH unit. The pK_a was then calculated using the well known Henderson – Hasselbach equation[14], by plotting log $[A^-] / [HA]$ vs. pH values. The intersection of the straight line with the pH axis at log $[A^-] / [HA] = 0$ gave the apparent pK_a directly. All experiments were carried out at room temperature, 25 ± 2 °C.

RESULTS AND DISCUSSION

With the exception of compound I_e ($m\text{–}NO_2$ substituent) the polarograms of the other members of the series studied displayed two polarographic waves (a) and (b) with equal wave–height in the potential range 0 to –2.0 V (vs. SCE). Schematic polarograms of 10^{-4} mol L^{-1}, 40 % V / V ethanolic buffers in the pH range $\sim$ 2–11 of I_a taken as a representative example is shown in Fig. 1. The more–positive 4e wave a predominates throughout the whole pH range with approximate constant wave height. On the otherhand the more negative (wave (b) at $pH > 5$ splits into two waves b_1 and b_2 of equal heights and at still higher pH's ($pH > 8$) decreases in height and practically disappear at $pH \geq 11$. Effects of varying mercury pressure and depolarizer concentration, at selected pH values indicate that the waves are mainly controlled by diffusion in the region where i_l is practically pH–independent. Tests of irreversibility of these waves through logaritmic analysis [log $(i / i_l - i)$ vs. f(E)] indicated that these processes are irre-

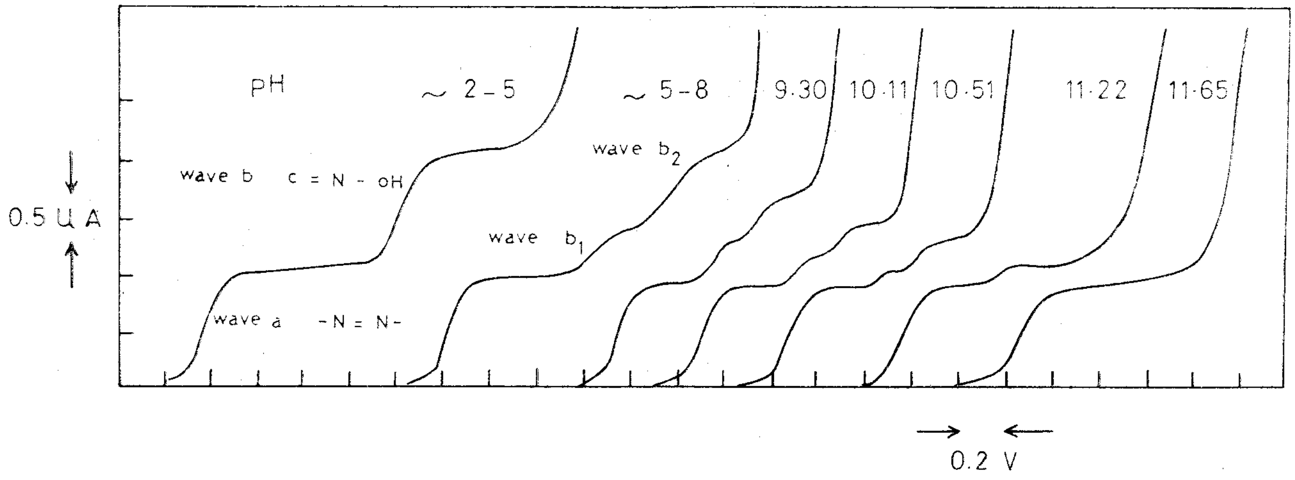


Fig. 1. Schematic representation of the polarograms of 10^{-4}M 2-phenylazo-1, 3-indandione-monoxime I_a in 40 % v/v ethanolic Britton-Robinson buffers.

versible in nature as shown by the values of transition and transfer coefficient given in table 1. The effect of pH on half–wave potentials $E_{1/2}$ and limiting current i_l of the waves are graphically illustrated in Fig. 2. As is clear $E_{1/2}$ of waves (a) and (b) are pH–dependent while waves (b_1) & (b_2) showed weak dependence.

Table 1. Polarographic data and spectrophotometric pK_a values for compounds I_{a-e}

Compound	$E_{1/2} = f(pH)$	$\frac{2.3\ RT^a}{\alpha n}$	αn^b	pH^c	Potentiometric $pK_a (\pm 0.05)$
I_a	$E^a{}_{1/2} = -0.22 - 0.065$ pH	0.067	0.883	3.21	11.25
	$E^b{}_{1/2} = -1.01 - 0.040$ pH	0.045	1.313	3.21	
I_b	$E^a{}_{1/2} = -0.240 - 0.070$ pH	0.070	0.837	3.16	11.28
	$E^b{}_{1/2} = -1.01 - 0.042$ pH	0.047	1.252	3.16	
I_c	$E^a{}_{1/2} = -0.280 - 0.067$ pH	0.069	0.853	3.20	11.19
	$E^b{}_{1/2} = -4.01 - 0.045$ pH	0.043	1.381	3.20	
I_d	$E^a{}_{1/2} = -0.210 - 0.054$ pH	0.064	0.913	3.10	11.42
	$E^b{}_{1/2} = -1.01 - 0.04$ pH	0.050	1.182	3.10	
I_e	$E^a{}_{1/2} = -0.105 - 0.045$ pH	0.051	1.150	3.25	11.06
	$E^b{}_{1/2} = -1.03 - 0.035$ pH	0.048	1.221	3.25	
	$E^c{}_{1/2} = -0.17 - 0.08$ pH	0.087	0.681	3.25	

a Slope of logarithmic analysis.

b Transition coefficient.

c Individual pH value at which logarithmic analysis was carried out.

The shilft of $E_{1/2}$ to more negative potentials with increase of pH of the solution for the waves ($E_{1/2} = f$ (pH)) is expressed by linear equation collected in table 1. The more positive wave (a) is assigned to reduction of the azo / hydrazo moiety while wave (b) is assigned to reduction of the oxime group in the molecule after splitting of the $N = N$ moiety. Proof of aniline in the sample after cpe at the limiting current of wave a (cf. experimental) is a direct evidence for the correctness of this assignment. At this point it seemed mandatory to ascertain further this conclusion via investigating the polarographic behaviour of the m–NO_2 derivative. Thus the polarograms of I_e (m–NO_2 substituent) were run and inspected in the whole pH range of study.

In addition to waves (a) and (b) of (I_{a-d}) compounde I_e showed an additional 4e irreversible diffusion–controlled wave (c) lying between waves (a) and (b). The effect of pH on $E_{1/2}$, also i_l–pH of the different waves is shown in Fig. 3. The behaviour of the additional wave (c) can be described by the linear equation, (cf. table 1). Since the behaviour of this wave is comparable to that for a m–nitro–group[19] it is not unreasonable to attribute this extra wave to the reduction of the nitro group to a hydroxyl amine

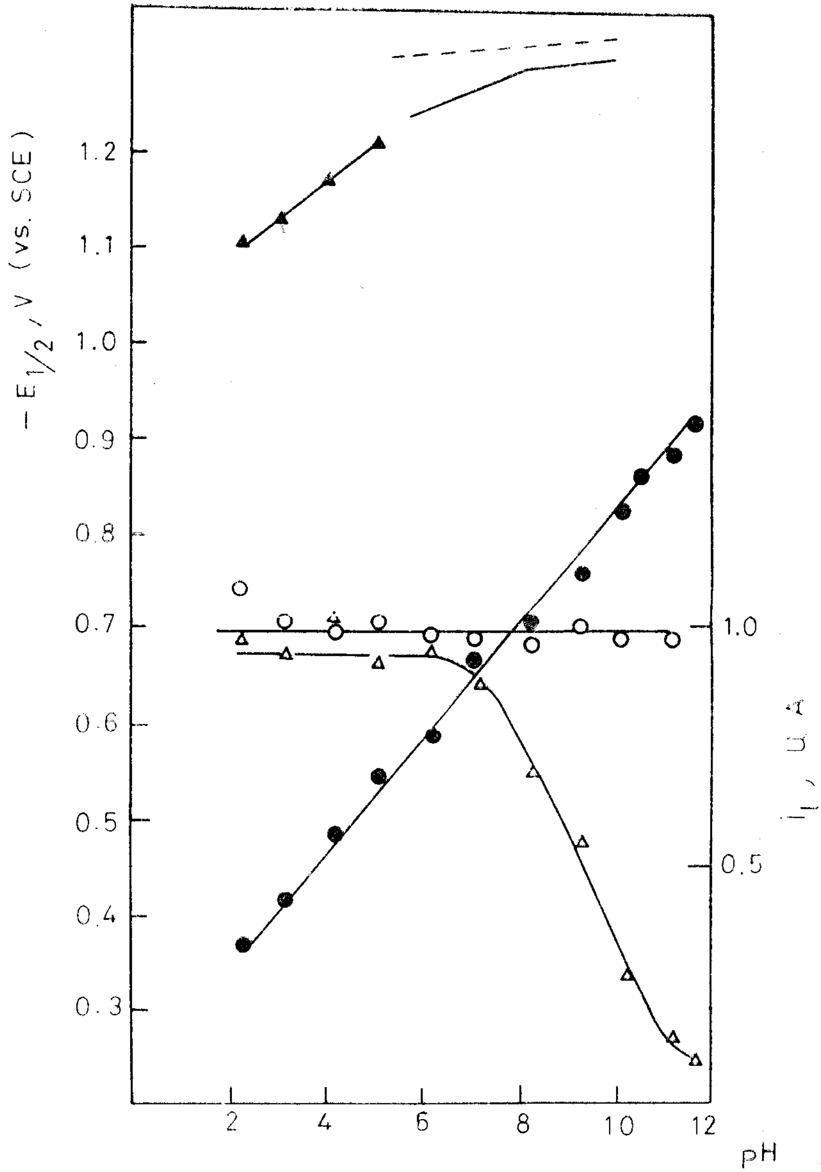


Fig. 2. Dependence of $E_{1/2}$ (O, △, —, - - -) and i_l (O, △) on pH for I_a: O, O wave a; △, △ wave b; — wave b_1; - - - wave b_2.

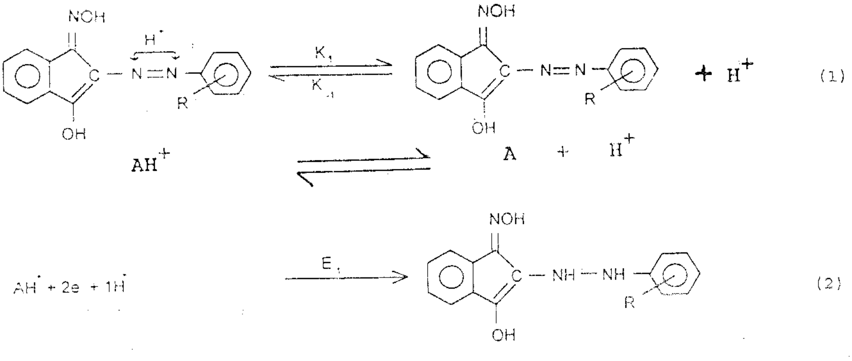
$$-NO_2 + 4e + 4H^+ \xrightarrow{EC} -NHOH + H_2O$$

Positive spot test for aniline to the product of cpe carried at the plateau of wave (c) indicates this wave is due to reduction of the nitro group in the separated m–nitro aniline formed during electrolysis at the more positive potential of wave (a). Since reduction of the functional group is prior to nitro group, an azo structure is this predominating[3, 7, 8]. Further evidence for this assignment will be revealed from structure energy relationship discussed later.

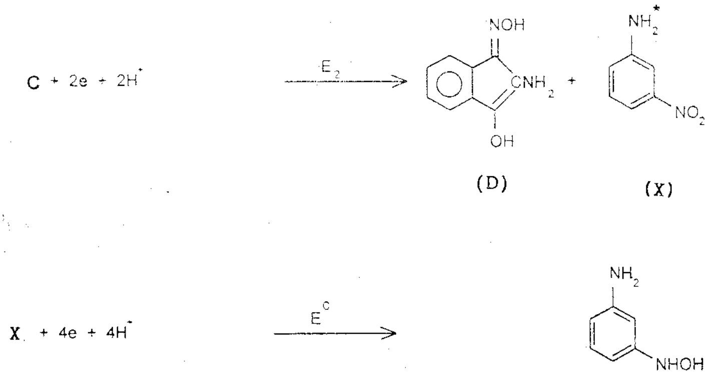
The $dE_{1/2} / d\,(pH)$ value of wave (a) assigned to reduction of the $N = N$ group is 0.065 V per pH unit, indicating that protons are involved in the electrode process. Applying the equation[20].

$$d\,E_{1/2} / d\,pH = -(0.059 / \alpha n)\,P^+ \tag{1}$$

the value of P^+ was found to be ≈ 1 (cf. Table 1) indicating that one proton is consumed; hence the rate of protonation is the rate determining step. This is to be expected since the azo bond is known to be reduced in the protonated form. Independence of i_l from pH for wave (a) indicates that surface protonation remains fast over the whole range of pH studied. $E_{1/2}$–pH plot (Fig. 2) indicates that one and the same form is reduced over the entire pH range studied. The results of cpe at the limiting current of wave (a) showed separation of aniline, a clear indication that the molecule has been reduced by saturation of the $N = N$ bond followed by cleavage. Scheme 1 is thought to be compatible with these results.



(C)



(3)

(4)

$E_1 \approx E_2 = E^{a}_{1/2}$

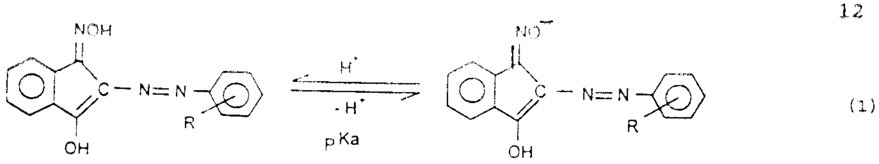
* Identified product

Scheme (1)

In case of compound I_e, instead of aniline, m–nitro aniline separates formed in step 3 which is reduced to the corresponding m–amino hydroxylamine in step 4.

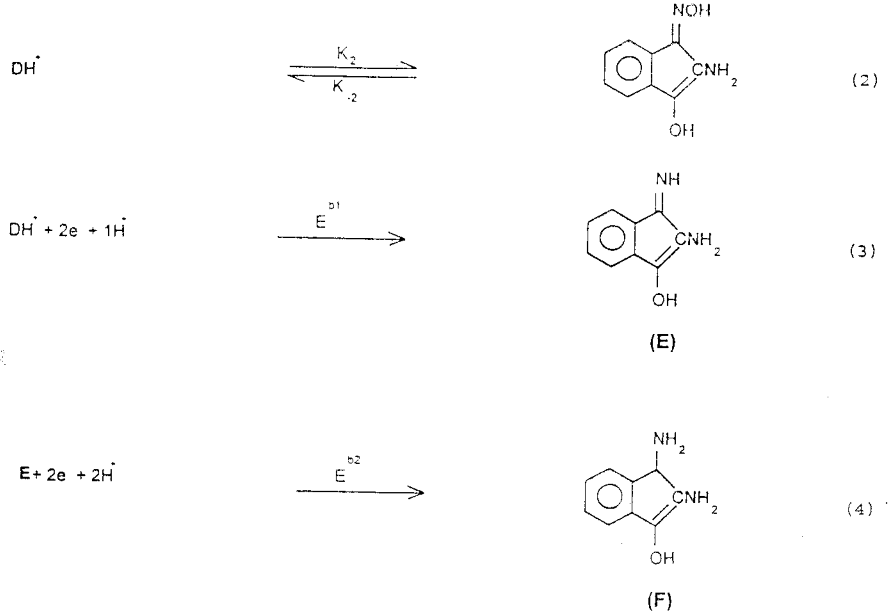
At $pH < 5$ the rate of the protonation of the oxime group in the molecule (resulting from spliting of the $N = N$ moiety) is fast enough) ($dE_{1/2} / dpH = 0.040$ for wave b). Moreover applying equation (1) is the number of protons (P^+) consumed in the rate determining step is one (0.88) per molecule. This evidence is a direct indication that the protonation precedes the electron uptake. At $5 < pH < pK_a$ wave (b) splits into two waves (b_1, b_2) of equal heights: the first is pH–dependent ($dE_{1/2} / dpH$ 0.040) while the second is practically pH independent. As the solution pH increases wave height starts to decrease and practically disappears at $pH \geq pK_a$.

At such low H^+ concentration the oxime groups is present in the less reactive anion–form. Scheme 2 provides an interpretation of these results:



(1)

At pH < 5



(2)

(3)

(E)

(4)

(F)

$$E^{b1}_{1/2} \approx E^{b2}_{1/2} = E^{b}_{1/2}$$

At 5 < pH < pKa

$$DH^{+} + 2e + 1H^{+} \xrightarrow{E^{b1}} (E)$$

$$E + 2e + 2H^{+} \xrightarrow{E^{b2}} (F)$$

$$E^{b1}_{1/2} \neq E^{b2}_{1/2}$$

Scheme (2)

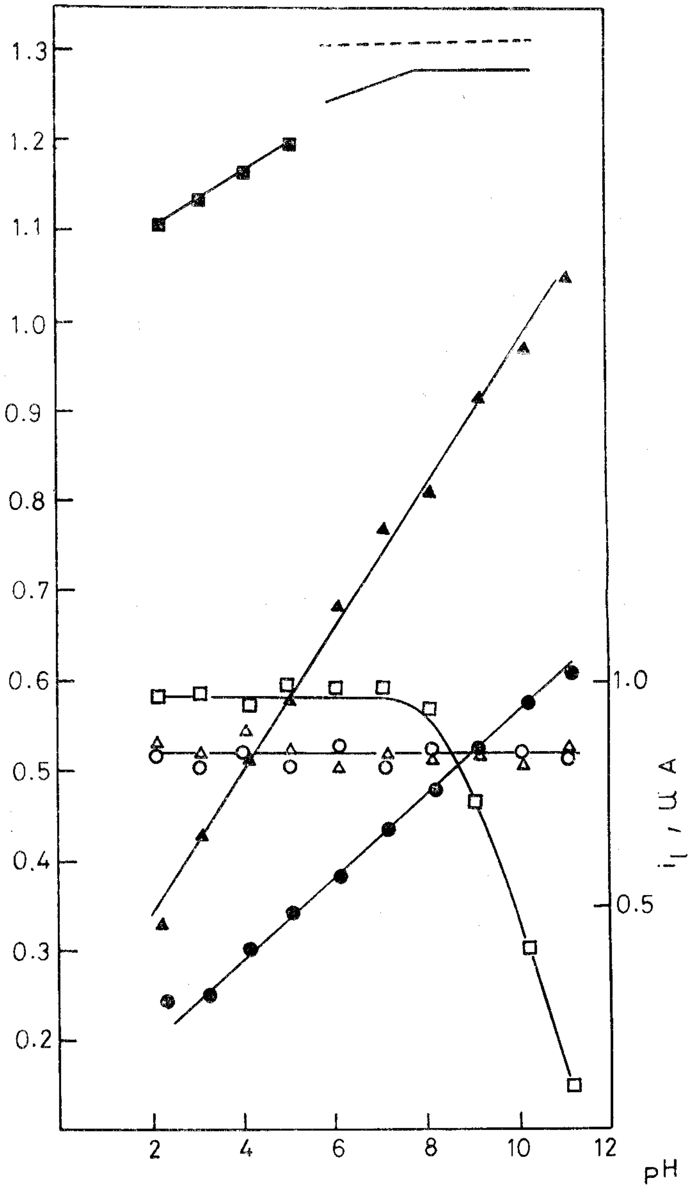


Fig. 3. Dependence of $E_{1/2}$ (O, △, —, ——, - - -) and i_l (O, △, ⊡) on pH for I_e: (O, O) waev a; (△, △) wave c; ($E_{1/2}$, ⊡) wave b, — wave b2; — wave b_1.

The aforesaid result indicates clearly reduction of the N = N functional group prior to the oxime group. This is contrary to previous report[12] where the oxime group is reduced first followed by the functional group which assigned a hydrazone structure –N = NH–. It may be concluded that if an oxime group in some location of the molecules is reduced before an azo / hydrazo form a hydrazone structure[12] prevails, while in case of an azo form the opposite takes place (present results).

Structure Energy Relation

Additional support for the proposed electroreduction diagrams seemed of value. Therefore, it appeared necessary to study the effect of substituents on the reaction sites (–N = N– and $>C = NOH$) of these molecules through $\sigma - E_{1/2}$, pK_a correlations.

The most reliable $E_{1/2}$ values for the reduction of –N = N– group at selected pH have been correlated with different Hammett σ constants[21] through statistical treatment of the data using Jaffe calculation[23] (Table 2). Representative $E_{1/2} - \sigma$ plots are illustrated in Fig. 4. The constancy of the transfer coefficient (αn)[23], a prerequisite for correlation, was checked by logarithmic analysis, αn was found to be practically constant.

Table 2. Results of the statistical treatment of the $E_{1/2}$–σ data (wave a) at different pH for compounds Ia_c.

pH	ρ^a	r^b	s.d^c	n^d
4	0.256	0.970	±0.0156	5
6	0.312	0.998	±0.0037	5
9	0.387	0.995	±0.0097	5

a reaction constant, b correlation coefficient, d number of points, c standard deviation calculated from[22].

$$s = \pm \left[\{\Sigma^2 - (\Sigma xy)^2/\Sigma x^2\}/n-2\right]^{1/2}$$

As is clear good linearity was obtained with positive ρ values varying between 0.256 and 0.387. These values are in accordance with those reported in literature for compounds containing the azo –N =N– group[23]. That the nitro–group is reduced after wave a is confirmed here by the fact that the point for m–NO_2 lies on the $E_{1/2} - \sigma$ curve but not that for m–NH OH (reduced form of the nitro group), an indication that the reducible –N = N– centre is influenced by a nitro– and not a hydroxylamine–group.

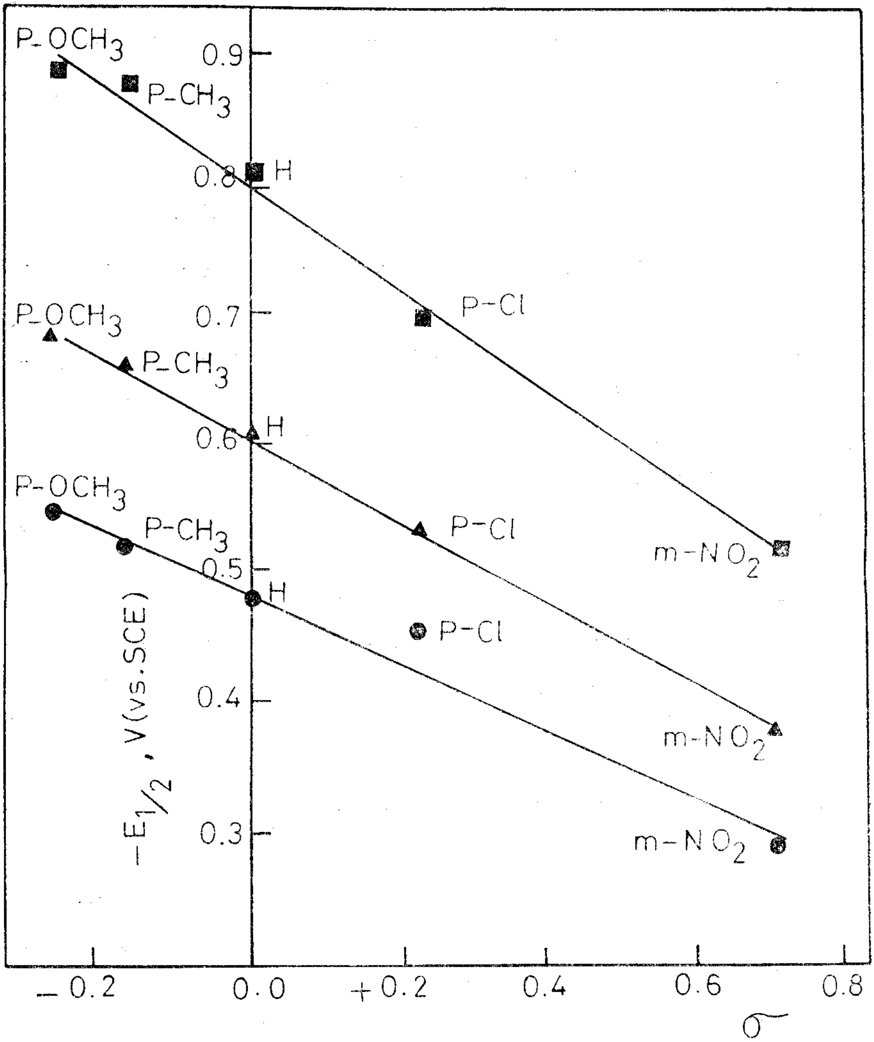


Fig 4. $E_{1/2}$–σ relation for 2-phenylazo, 1–3–indandione-monoxime derivatives at different pH values: o pH 4; △ pH 6; ■ pH 9.

On the otherhand trials to correlate pK_a values quoted in table 1 to different σ sets (σ, σ°, σ^+) showed no dependence. This is to be anticipated since ionization arises at the oxime group (step 1 Scheme 3) which is sufficiently far from the substituent in the phenyl ring.

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