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ELECTROCHEMICAL AND ESR STUDIES ON THE REDUCTION OF SOME INDOLINONE DERIVATIVES AND OF THEIR N-OXIDES IN DMF

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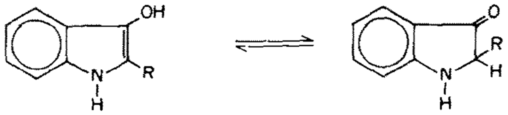
Abstract—2-Phenyl-3-oxo-3H-indole **4** and 3-imino-, 3-iminoxy-, derivatives, the corresponding N-oxide **3**, and 2-phenyl- **5** and 2-(2'-pyridyl-) isatogen **6** have been reduced in DMF and in DMF in presence of proton donors, and followed by polarography, controlled potential coulometry, cyclic voltammetry, UV, and ESR. In aprotic media, compounds **1**, **4**, **5** and **6**, are reduced via anion radical intermediates.

In the course of our previous researches on the electrochemical reduction of 3-arylimino-3H-indole N-oxides[1,2] we showed that in aprotic medium the process follows two mono-electronic steps, the first leading to an anion radical, as proved by ESR,[2] the second to the diamagnetic dianion. When the reduction is carried out in the presence of proton donors (such as benzoic acid and monochloroacetic acid) it follows a two step process, the former, more positive, leading to the formation of the N-hydroxy-derivatives, the latter to the formation of a mixture of 1 - hydroxy - 2 - phenyl - 3 - arylamino - indoles and of 2 - phenyl - 3 - arylamino - indoles, the relative ratio depending from the substituent in the *p*-position in the 3-phenyl ring. Such results are not in full agreement with results of the chemical reduction,[3,4] leading to 3 - arylamino - indoles.

In order to obtain more information on the influence of the substituent in determining the direction of the electrode process, the investigation has been extended to the N-oxides **3**, **5** and **6**: compounds **1**, **2** and **4** have also been considered as possible reaction intermediates. While there has been no report of the electrochemistry of compounds **1**–**6** in non-aqueous media, the polarographic behaviour of 2-phenyl-isatogen **5** and 2,2'-pyridyl-isatogen **6** in buffer-dioxan mixtures as solvent has been reported.[5] The reduction mechanism, proposed by analogy with the single four-electron step reduction of the related nitrone system in aqueous solution, would give indolones which would be further reduced to indoxyls **7**.



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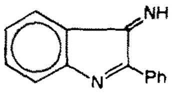
R = phenyl
R = 2-pyridyl

We now report our work related to isatogens **5** and **6**, which are shown to possess *in vitro* antibacterial properties,[6] in DMF and in DMF with protonating agents of various strengths. Polarography, cyclic voltammetry, controlled potential electrolysis as well as ESR and UV spectrometry were the techniques used.

EXPERIMENTAL

Compounds **1** and **4**,[7] **2**,[8] **3**,[9] **5**[10] and **6**[11] have been prepared following the literature. N,N-Dimethylformamide (Merck, spectrophotometric grade) was purified as previously described.[12] The water content of the solvent was determined as 0.005% by Karl



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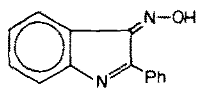

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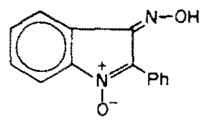

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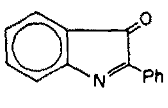

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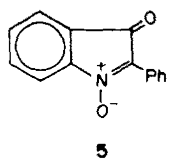

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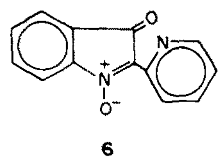

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Fisher titration. Tetraethylammonium perchlorate (Et_4NClO_4) (Erba, RS grade for polarography), was vacuum dried at 60°C for 4 days. All the other products were AR grade. Argon (99.995% pure) used to deoxygenate the solutions under examination, was passed through a DMF solution containing Et_4NClO_4 and depolarizer at the same concentration as the test solution. The polarograms and the cyclic voltammograms were recorded using the apparatus and the cell previously described.[2] The reference electrode was Hg/Hg_2Cl_2, NaCl (sat aq)/agar-NaCl(aq)/agar (1.5% w/v) DMF-water (40% v/v) Et_4NClO_4 (sat)/methyl cellulose (5% w/v)-DMF-Et_4NClO_4 (sat)/sintered-glass disc. Its potential was 0.045 V vs the aqueous SCE, liquid junction potential being included. The dropping mercury electrode (DME) with the forced separation of the drop had the following characteristics: $m = 0.208\,mg\,s^{-1}$, $t = 2.0\,s$ at $h = 90.0\,cm$, $T = 20.0°C$ in DMF-Et_4NClO_4 0.1 M. The controlled potential coulometry was carried out using the apparatus previously described.[12] UV Spectra were recorded on a Unicam SP 800 spectrophotometer. Throughout all measurements the temperature was kept constant within 0.1°C. The accuracy of half-wave potentials, reported in Table 1, is within the range of ± 5 mV. ESR spectra were recorded either on a Jeol JES-PE-1X or in a Varian E-4 ESR spectrometer at room temperature. After the electrolysis was performed the solution (about 1×10^{-3} M) was transferred under vacuum into a cell for aqueous samples and the cell transferred into the spectrometer cavity. Chemical reduction of compounds **1**–**6** was performed directly in the cell as previously described.

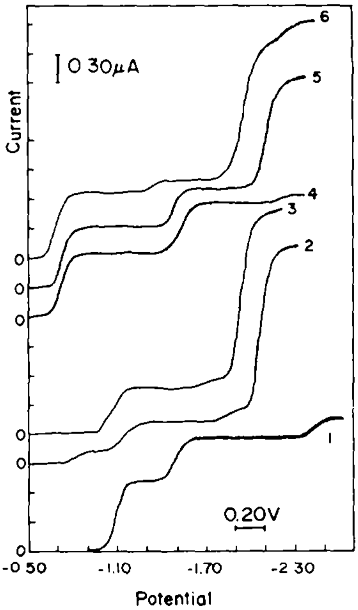

Fig. 1. Polarograms of indolinone derivatives **1**–**6** in DMF-Et_4NClO_4. (The experimental conditions are reported in Table 1).

RESULTS

Voltammetric methods

Aprotic media. The polarographic behaviour at the DME of indolinone derivatives **1**–**6** in DMF (with Et_4NClO_4 as supporting electrolyte) is shown in Fig. 1. In Table 1, half-wave potentials ($E_{1/2}$) and other polarographic data are reported. The limiting currents of the first, for compounds **1**, **3**–**6**, the second, for **3**, **4**, and the third reduction step, for **5**, are proportional to the depolarizer concentration (examined range 1×10^{-4}–5×10^{-3} M). Moreover, the limiting currents of every polarographic wave have a temperature coefficient of 1.0–1.5% per degree in the range 15–30°C. The limiting current of the oxime **2** first reduction step is neither proportional to oxime concentration not does it vary linearly with the square root of the mercury head. Moreover, by addition of 0.015% polyvinylchloride (PVC) this first wave completely disappeared; at the same time the height of the second polarographic wave reached the first wave value of 2-phenylisatogen oxime **3**, but no change occurs in third wave and in total height of the polarogram, that leads us to conclude that the first wave is characteristic of an adsorption pre-wave.

Cyclic voltammograms at the hanging mercury drop electrode of **1**–**6** in DMF-Et_4NClO_4 are given in Figs. 2 and 3. Indolenine **1** exhibits two cathodic and two anodic peaks (Fig. 2, 1a): the first step shows a clear corresponding anodic peak (Fig. 2, 1c), but the first anodic step decreases and finally disappears (Fig. 2, 1b–c) if the potential span is gradually restricted up to − 1.10 V (vs mercury pool). The oximes **2** and **3** cyclic voltammograms show three and two cathodic peaks respectively, but only one anodic peak (Figs. 2,2a and 2,3a respectively) which disappears when the potential is scanned positive of − 1.1 to 1.2 V (Figs. 2,2b and 2,3b). Moreover, by addition of PVC to the solutions of the oxime **2** the second cathodic step increases but the first one (adsorption pre-wave) disappears (Fig. 2,2c). In the potential sweep voltammetry indolinone **4** gives two cathodic and two anodic peaks, which appear to be reversible (Fig. 3,4a–b). Finally, isatogens **5** and **6** exhibit three cathodic peaks, corresponding to the three polarographic waves, but with two (Fig. 3,5a–c) and one (Fig. 3,6a–c) anodic peak respectively, which all appear reversible. For compounds **1**, **4**–**6** the separation between the first cathodic and the corresponding anodic potentials is close to the theoretical value for a reversible one-electron transfer.[13] Moreover, in the range of the scan rate used ($v = 0.06$–1.00 V/s),

Table 1. Polarographic data for the reduction of indolenine derivatives **1**–**6**[a]

Compound	$-E'_{1/2}$ (V)	i'_d (μA)	$\frac{\log i'_d}{\log h}$	I_d[b]	slope[c] (mV)	$-E''_{1/2}$ (V)	i''_d (μA)	$\frac{\log i''_d}{\log h}$	$-E'''_{1/2}$ (V)	i'''_d (μA)
1	1.096	0.72	0.45	1.88	57.0	1.487	0.45	0.57	2.451	0.19
2	0.800[d]	0.12				1.107	0.32	0.45	2.058	1.82
3	1.058	0.47	0.58	1.10	79.0	1.920	1.84	0.61		
4	0.724	0.66	0.50	1.63	67.1	1.518	0.52	0.55	2.194	0.90
5	0.728	0.62	0.50	1.58	59.2	1.467	0.38	0.58	2.099	1.18
6	0.682	0.67	0.45	1.72	63.2	1.354	0.13	0.30		1.66[e]

[a] Solutions in DMF-Et_4NClO_4 0.1 M with about 1.10^{-3} M depolarizer; $t_g = 2.0$ s; $h = 90.0$ cm; $T = 20.0°C$.

[b] $I_d = i_d/m^{2/3}\,t^{1/6}M$.

[c] Slope was calcd. using $E_{1/4} - E_{3/4}$ values.

[d] Adsorption pre-wave.

[e] Mixed wave.

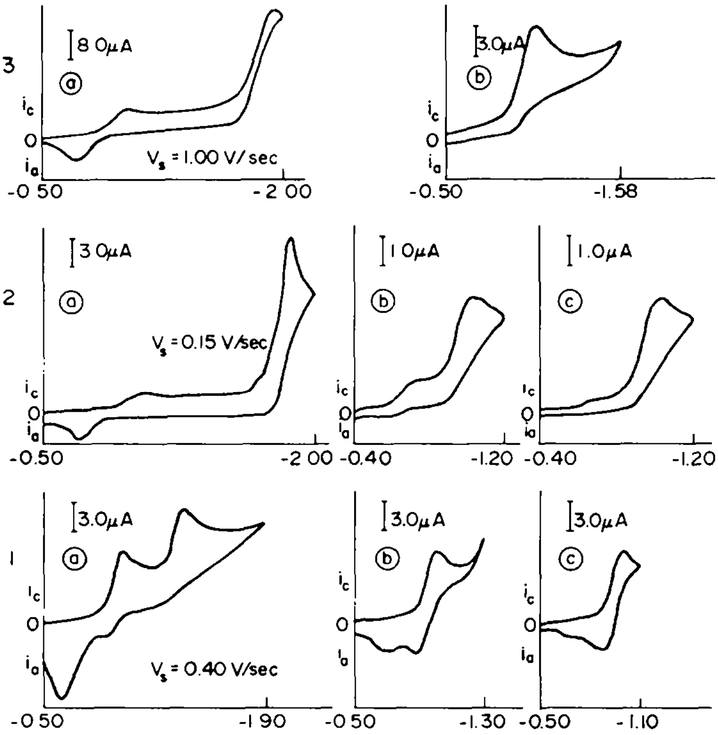

Fig. 2. Cyclic voltammograms of about 5 × 10^{-4} M indolinone derivatives **1–3** in DMF-Et_4NClO_4 0.1 M at the scan rates (Vs) indicated. (a) Potential span including all polarographic waves; (b) and (c) potential span restricted to that of the first wave. For oxime **2**, the voltammogram (c) is as (b) with about 0.01% PVC. (Hanging drop 0.5 μl; T = 22.0°C; mercury pool reference electrode).

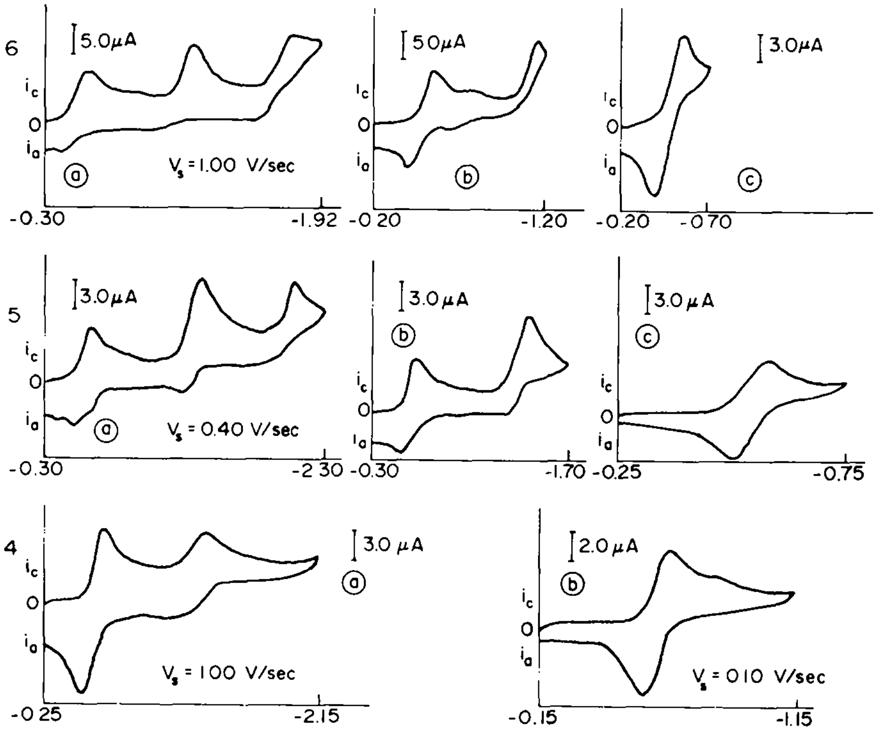

Fig. 3. Cyclic voltammograms of about 5 × 10^{-4} M indolinone derivatives **4–6** in DMF-Et_4NClO_4 0.1 M at the scan rates (Vs) indicated. (a) Potential span including all polarographic waves; (b) and (c) potential span restricted to that of the second (isatogens **5**, **6**) and first wave. (Hanging drop 0.5 μl; T = 22.0°C; mercury pool reference electrode).

peak potentials are essentially independent of the scan rate and the ratio anodic to cathodic peak currents is close to unity. These facts are indicative of an electron transfer process for the first reduction step relative to **1**, **4**–**6**, producing a species which is stable during the time of the measurements. The existence of intermediate anion radicals is confirmed by strong ESR signals.

Protic media. In order to elucidate the reaction mechanism, the reduction of **1**–**6** in DMF/Et_4NClO_4 with protonating agents of various strengths, such as water, 3,4-dimethylphenol, benzoic acid, monochloroacetic acid, etc. has been studied. When increasing quantities of 3,4-dimethylphenol ($pK_d > 15$) are added to solutions of indolenine **1** the first original wave increases at the expense of the other waves; at the same time its potential ($E_{1/2}$) shifts to more positive values ($\Delta E_{1/2} = 100$ mV, with protonating agent/substrate **1** mole ratio, $r = 4$). For ratios $r > 4$ the polarogram shows a unique reduction wave ($E_{1/2} = -0.94$ V, for $r = 10$), the height of which doubles the value of the first wave found in aprotic medium. Using water as protonating agent, much larger mole ratio values are needed to obtain similar results (for $r > 5000$, a unique reduction step occurs). Addition of dimethylphenol even in excess amount, to solutions of **2**–**6** has no effect, either on the limiting current or on the half wave potentials of the first (prewave and main wave, for oxime **2**) original waves, but it causes the other waves be gradually replaced by a new reduction step ($E_{1/2} = -1.00$ V when $r = 10$ for compounds **5** and **6**, and $r = 20$ or 30 for oximes **2** or **3** respectively). The r values for which the polarograms show only two reduction waves vary in the following sequence $\mathbf{3} > \mathbf{2} \simeq \mathbf{5} > \mathbf{6} > \mathbf{4}$; for 2-phenylisatogen-oxime **3**, $r = 30$, but for 3 - oxo - 2 - phenylindolenine **4**, $r = 1.5$. Moreover the polarogram of oxime **3** exhibits also an increasing (about 25%) of the total height. Further addition of protonating agent to solutions of **2**–**6** causes the increase of the indolinone **4** first wave, at the expense of the last, and the shift of the second wave (second and third for oxime **2**) of other compounds to more and more positive potentials. In the presence of enough amount of dimethylphenol ($r > 20$ for indolinone **4**, but $r > 200$ for other compounds) the corresponding polarograms exhibit a single reduction step. The addition of increasing quantities of water, as weaker protonating agent, to the solutions of oximes **2**, **3** causes the last reduction wave to shift to more positive potentials. With H_2O/oxime mole ratio values large enough ($r > 15{,}000$ and $r > 25{,}000$ for oxime **2** and **3** respectively) the corresponding polarograms show a single reduction wave. The addition of water to the solution of indolinone **4** has no effect on the first reduction step, but it causes a decrease of the limiting current and a shift of the second step to more positive potential ($\Delta E_{1/2} = 20$ mV; $\Delta E''_{1/2} = 350$ mV and $\Delta i''_d = 15\%$ with $r = 800$). The polarograms of the solution of isatogens **5**, **6** with water as proton donor, show that the second wave increases at the expense of the third, while both waves shift to more positive potentials. In the presence of a sufficient amount of water ($r > 20$–$30{,}000$) compounds **4**–**6** give a single reduction step. The addition of a stronger protonating agent, such as monochloroacetic acid† ($pK_d = 10$), produces a new wave at more and more positive potentials than the original reduction step of 2-phenyl 3-iminoindolenine **1**. The original waves gradually decrease while the new increase so that for $r > 3$ the polarogram exhibit a single reduction step ($E_{1/2} = -0.20$ V for $r = 20$), the height of which is approximately equal to the overall limiting current measured in aprotic medium. By addition of acid ($0 < r < 3$) to oxime **2** the second original wave increases at the expense of the third, the $E_{1/2}$ remaining practically unchanged; at the same time the first wave increases and shifts to more positive potentials ($E_{1/2} = -0.60$ V for $r = 20$) so that for $r = 3$ the polarogram shows only two reduction steps ($i''_d/i'_d = 3.2$). Further addition of acid causes the first wave to increase; for $r > 50$ a single reduction step is observed and its limiting current is equal to the original overall limiting current. When monochloroacetic acid ($0 < r < 3$) is added to 2-phenylisatogen oxime **3**, the first wave increases at the expense of the second, the $E_{1/2}$ remaining practically unchanged, so that, for $r = 3$, they form a single wave. For the molar ratio values $r > 3$ the last is gradually replaced by a new ill-separated wave ($E_{1/2} = -0.85$ V for $r = 20$); at the same time the polarogram exhibit also an increasing (about 45% of the overall limiting current. Finally, the polarograms of indolinones **4**–**6** with monochloroacetic acid show a new wave, at more positive potentials, which increases as mole ratio r increases, at the expense of other original waves. For $r > 2$ a single reduction step is observed (when $r = 3$, $E_{1/2} = -0.25$ V, -0.55 V and -0.32 V for **4**, **5** and **6** respectively). It is important to notice that by successive additions of a proton acceptor such as tetraethylammonium hydroxide to the solution of oxime **2** or **3** in DMF–Et_4NClO_4, the first polarographic wave (prewave and main wave for **2**) lowers and finally completely disappears while the height of the second original wave raises to reach the value of the overall height of the polarogram, its half-wave potential remaining practically unchanged.

Controlled potential coulometry and spectrometry

Protic media. Coulometric determinations of indolinone derivatives **1**–**6** in DMF–Et_4NClO_4 with different quantities of monochloroacetic acid ($30 < r < 80$) were performed at the potentials of the single reduction step plateau. The number of electrons per molecule involved in the reduction of **1**, **2** and **3** was two, four and six respectively. The spectral absorption curves ($\lambda'_{max} = 312$ nm, $\epsilon' = 10{,}100$; $\lambda''_{max} = 354$ nm, $\epsilon'' = 11{,}000$) and the polarograms of the resulting colourless solutions were all identical. In the reversal coulometries (oxidations) two electrons per molecule of depolarizer were used up; the spectral absorption curves ($\lambda_{max} = 400$ nm, $\epsilon = 3070$) and the polarograms of the resulting yellow solutions showed clearly that 2 - phenyl - 3 - iminoindolenine **1** is produced. Moreover, both reduction of **1** and oxidation of the colourless solutions caused the formation of a cathanodic system. Controlled potential electrolysis of indolinones **4** and **5** involved two and four electrons per molecule respectively and gave colourless solutions ($\lambda'_{max} = 322$ nm, $\epsilon' = 16{,}800$; $\lambda''_{max} = 340$ nm, $\epsilon'' = 16{,}950$); in the subsequent oxidations two electrons per molecule were used, indolinone **4** being the oxidation product ($\lambda_{max} = 430$ nm, $\epsilon = 2400$). Finally, the coulometric determinations of isatogen **6** involved four and two electrons per molecule in the reduction ($\lambda'_{max} = 326$ nm, $\epsilon' = 14{,}100$; $\lambda''_{max} = 356$ nm, $\epsilon'' = 13{,}700$) and in the subsequent oxidation respectively ($\lambda_{max} = 406$ nm, $\epsilon = 2350$). Both the reduction of the indolinone **4** and the oxidations of the electrolysed indolinones **4**, **5** gave rise to a cathanodic system ($E_{1/2} = -0.15$ V, when $r = 40$). Likewise, the oxidation of

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†In the presence of monochloroacetic acid, benzoic acid, etc. the polarograms of indolinone derivatives **1**–**6** exhibit maxima and droptime irregularities.

the electrolysed solution of 2 - (2' - pyridyl -)isatogen **6** caused the formation of a cathanodic system ($E_{1/2} = -0.10$ V, when $r = 40$).

Aprotic media. Coulometric determinations of **1–6** in DMF/Et_4NClO_4 at potentials corresponding to the plateau of the first polarographic wave were recorded, in order to check if some ESR signal, corresponding to radicals formed during the electrochemical process, could be detected. As a matter of fact radical $\mathbf{4}^{\cdot -}$ (see the following discussion for symbol) is obtained from reduction of **1** and **4** probably via an hydrolysis of the 3-imino group in the case of **1**; spectrum reported in Fig. 4 is attributed to this radical. In the same way were obtained radicals $\mathbf{5}^{\cdot -}$ (see Fig. 5) with $a^N = 5.85$ gauss for one nitrogen and $\mathbf{6}^{\cdot -}$ (see Fig. 6) with $a^N = 6.28$ gauss for one nitrogen, $a^H = 1.40$ gauss for two equivalent hydrogens (the two *o*-, *p*-benzo protons) and with some additional splitting due either to the *m*-benzo protons or to the protons of the 2-pyridyl substituent. The reduction of compound **1** gave values of $n_{app} > 1.5$ faradays per mole and the electrolysis current decayed to a value higher than that of the corresponding back-ground current. The polarograms recorded during the electrolysis show that a decrease of the second wave corresponds to a decrease of the first one. As the electrolysis goes on the ESR signal intensity slowly decreases and finally the signal disappears.

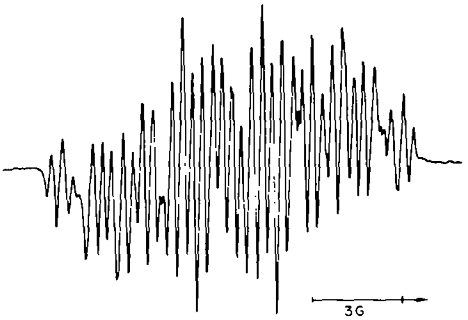


Fig. 4. Experimental ESR spactrum attributed to anion radical $\mathbf{4}^{\cdot -}$.

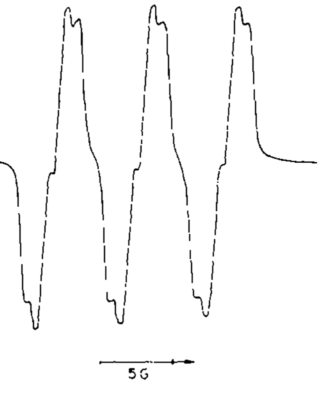


Fig. 5. Experimental ESR spectrum attributed to anion radical $\mathbf{5}^{\cdot -}$.

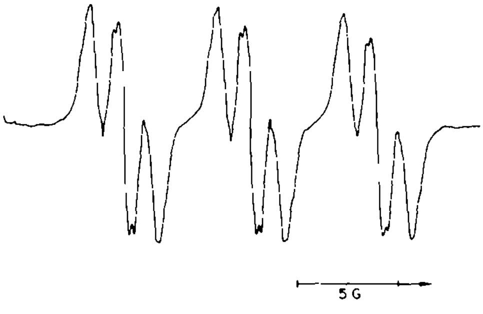


Fig. 6. Experimental ESR spectrum attributed to anion radical $\mathbf{6}^{\cdot -}$.

The oximes **2** and **3** uses up 0.8–1 electrons per molecule and the polarograms registered during the electrolysis show that the second wave raises a little when the first decreases: in this case no ESR signal can be detected even if the reduction is carried out directly within the spectrometer cavity. These results are in accord with the ones obtained during the corresponding cyclic voltammetry experiments (see Figs. 2.2 and 3). It is noticeable to observe that the reduction leads to a compound identical to the one obtained by treating a DMF solution of the oxime with t-BuOK as showed by UV spectra. Further reduction at the potential corresponding to the second polarographic wave (−2.2 V) uses up four electrons per molecule for compound **2** and about six electrons for compound **3** and leads in both cases to 3 - amino - indole, as showed by UV spectra. The same results are obtained when the reduction is carried out on compounds **2** and **3** at −2.2 V, with n_{app} ranging from 4.7 to 4.9 and 6.7 to 6.9 faradays per mole respectively.

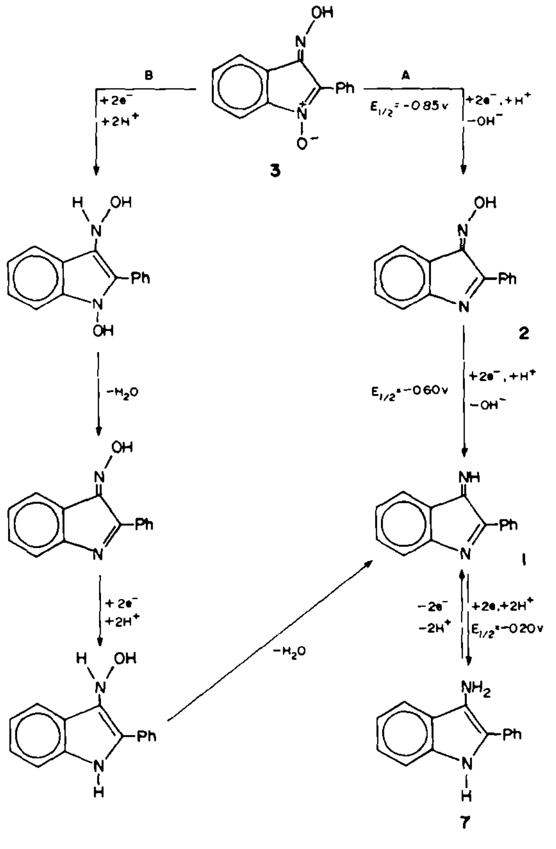
The indolinone **4** and the isatogens **5** and **6** uses up one electron per molecule of depolarizer: the polarograms registered during the electrolysis show the formation of a cathanodic system and an increase of the second wave to the expense of the third one, that is strongest in the case of **6** than in **4**. When the solution of **5** is further reduced at a potential corresponding to the second polarographic wave (−1.7 V) and then transferred into the ESR cavity, the signal obtained clearly demonstrates that the same radical formed in the mono-electronic reduction of **4**, has been obtained.

DISCUSSION

Compounds 1–3

The results of polarographic, coulometric and spectrometric measurements suggest that in DMF–Et_4NClO_4 and in the presence of a large excess of proton donors ($20 < r < 80$) like monochloroacetic acid compounds **1–3** can be reduced to 2 - phenyl - 3 - amino - indole **7** following either path **A** or **B** of the following Scheme 1. But, whilst the mechanism involving the π system, previously suggested for the reduction of 2 - phenyl - 3 - arylamino - 3H - indoles mono - N - oxides,[1] has no experimental support in this case, the one involving the N-oxide group on compound **3** (path **A**) is supported by the observation that $E_{1/2}$ of **3** is higher than $E_{1/2}$ of **2** and that in DMF and in the presence of monochloroacetic acid the 3 - indolyl - 3H - indoles mono - N - oxides, where a dehydration reaction has been observed, have values of $E_{1/2}$ identical to that of the corresponding 3 - indolyl - 3H - indoles.[14] A similar mechanism has been already proposed for the reduction of the nitrones[15] and of azoxybenzenes.[16] In the same way and on the basis of an analogous difference between $E_{1/2}$ of the oxime **2** and of the imine **1** one can suggests the reduction of **2** to **1** involves the oximino group more likely than the conjugated double bond system. It must be noted that the electron transfer at the electrode can be preceded by and/or be simultaneous to a fast protonation reaction, that cannot be demonstrated because the absorption spectra of **1**, **2** and **3** show no remarkable variations when recorded in presence or not of monochloroacetic acid.

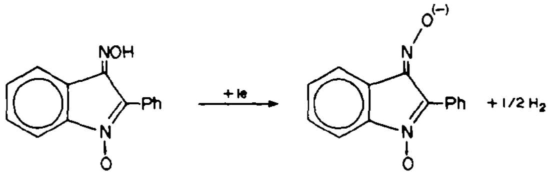
The reduction in aprotic medium of compound **1** involves the π system and leads to the formation of the



Scheme 1.

mono-anion radical, as the observation of an ESR signal demonstrates; the mono-anion is then reduced to the diamagnetic dianion. In the presence of a weak protonating agent a protonation occurs, that lowers its activation energy so that the reduction occurs at the potential of the first polarographic wave, which is now bielectronic. The ability of the anion radical to abstract protons from any protonic source (SH) present in DMF, like traces of water or DMF itself, explains why two electrons are used up during the electrolysis at a potential corresponding to the first wave.

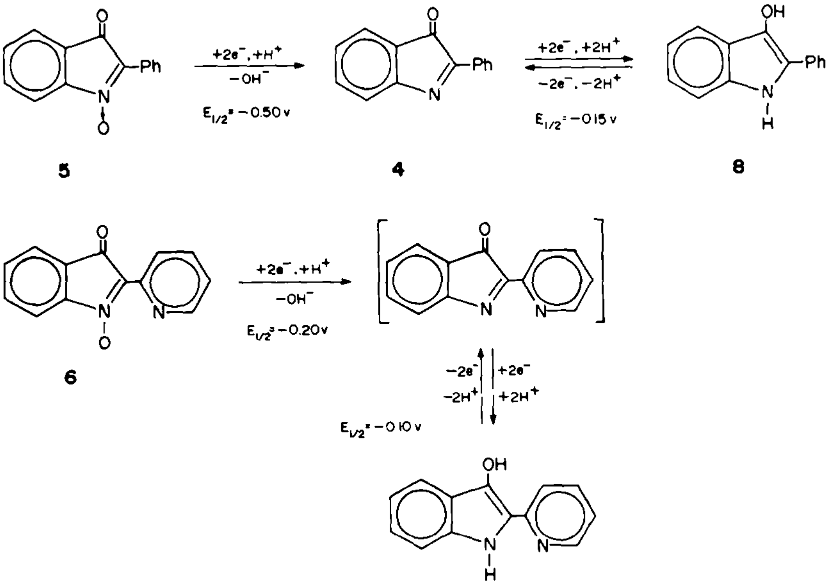
The absence of any radical signal concerning oximes **2** and **3**, during the reduction at potentials corresponding to the first wave, and the effect of the proton acceptor on the first polarographic wave (prewave and main wave for **2**) lead us to suggest a mechanism similar to that proposed for the reduction of 5- and 8-hydroxyquinolines in DMF.[17]



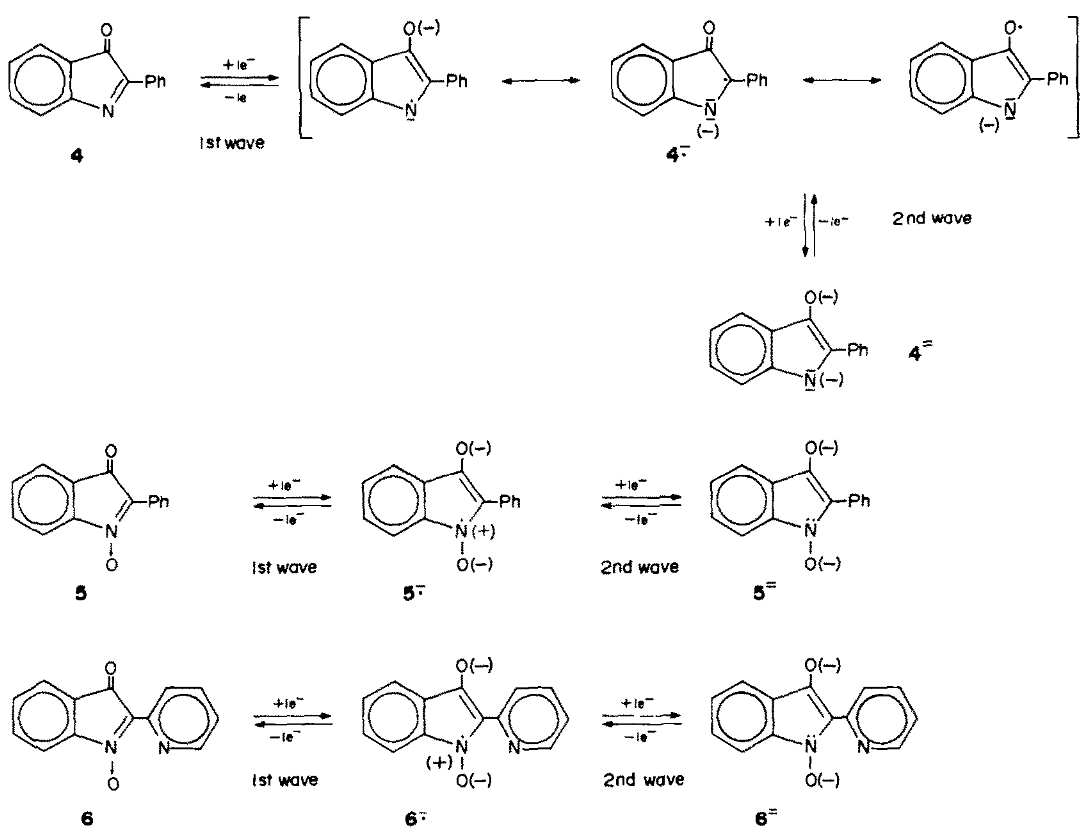
In such mechanism the first polarographic wave corresponds to the hydrogen discharge of the oxime group, while the second wave corresponds to the reduction of the conjugated double bond system in the oxime **2** or **3** anion and leads to 3 - amino - 2 - phenylindoles, after protons from the solvent have been used: the low availability of protons accounts for the experimental observation that the second wave for the reduction of **3** has about the same height of **2**, while the coulometry uses up six and four electrons per molecule respectively. When weaker protonating agents like water or 3,4-dimethylphenol are added, the reduction takes place at less negative potentials and the height of the wave for compound **3** increases of about 25%. It follows obviously from the proposed mechanism that the addition of the previous cited protonating agents does not affect the first wave.

Compounds 4–6

By analogy with the previous reduction of **3** to **2**, we suggest the first reduction step on compound **5** follows a path **A** type mechanism, that involves a deoxygenation reaction leading to compound **4**, that bears a two electron reduction to **8** (with r = 40). The same reaction sequence is suggested for the reduction of pyridyl-isatogen **6**, following Scheme 2.



Scheme 2.

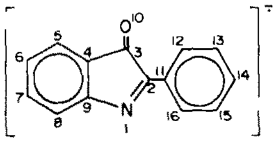


Scheme 3.

In aprotic medium the reduction process for **4**, **5** and **6** begins at the DME with a reversible mono-electronic step leading to the formation of anion radicals $\mathbf{4}^{\overline{\cdot}}$, $\mathbf{5}^{\overline{\cdot}}$ and $\mathbf{6}^{\overline{\cdot}}$ following Scheme 3.

While the interpretation of the spectra corresponding to radicals $\mathbf{5}^{\overline{\cdot}}$ and $\mathbf{6}^{\overline{\cdot}}$ does not require any discussion owing to their simplicity, the ESR spectrum attributed to radical $\mathbf{4}^{\overline{\cdot}}$ asks for further investigation. A spin density distribution calculation, using parameters reported in Table 2 and supposing coplanarity between the phenyl ring and the heterocyclic molecule, shows that the highest splitting constants must be attributed to hydrogens in *o*- and *p*-position on the phenyl ring, followed from the one in *o*- and *p*-position with respect to the carbonyl in the phenyl ring. The smallest hfsc shown by the spectrum asks for a couple of equivalent protons with $a^H = 0.35$ gauss. If one applies the McConnell formula $a^H = Q \cdot \rho_c$ (where $Q = 25$ gauss, $\rho_c = 0.0181$ and $\rho_{c_8} = 0.0110$, from Table 2), a theoretical value $a_6{}^H = a_8{}^H = 0.37$ gauss can be averaged, which is in good agreement with the experimental one. The synthesis of phenyl-substituted derivatives of **4** is in progress, in order to interpret the spectrum fully.

Table 2. Spin density distribution for radical $\mathbf{4}^{\overline{\cdot}}$



Position	McLachlan spin densities	Parameters
1	0.0611	$\alpha_N = 1.2$
2	0.3088	
3	0.1426	$\alpha_O = 1.5$
4	0.0239	
5	0.0244	$\beta_{CN} = 1.2$
6	0.0181	
7	0.0312	$\beta_{CO} = 1.6$
8	0.0110	
9	0.0387	$\beta_{cc} = 1.0$
10	0.1889	
11	−0.0345	$\lambda = 1.2$
12–16	0.0827	
13–15	−0.0292	
14	0.0786	

The second polarographic wave height (see Fig. 1 and

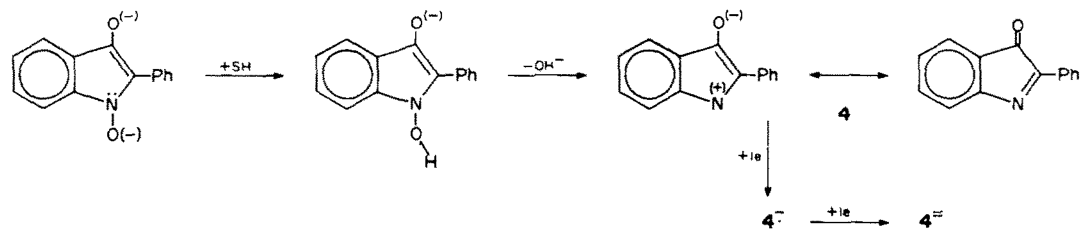


Table 1) that is relative to the formation of the dianions $4^{=}$, $5^{=}$ and $6^{=}$ shows the order $4 > 5 > 6$, that can mean a corresponding different availability of the anion radical to further reduction. This fact can be explained with the observation that $4^{\overline{\cdot}}$ can present at the electrode reactive sites that are still weakly charged, what cannot happen in the anion nitroxides $5^{\overline{\cdot}}$ and $6^{\overline{\cdot}}$. This interpretation agrees with the observation that the second wave increases its height when either in the bulk of the solution large amounts of anion radical are present (after the electrolysis at the potential of the first polarographic wave is exhaustive) or the small amount of water to the interface modifies the negative charge distribution of the anion.

The fact that four electrons per molecule are used up when the reduction of **5** is carried out at the potential corresponding to the second wave (− 1.7 V), the system being now not reducible further, can be explained with the reaction sequence which is confirmed by the observation of an ESR signal corresponding to $4^{\overline{\cdot}}$ when the solution is transferred into the ESR cavity. The previous sequence is also in accord with the fact that only two polarographic waves are shown from **5** and **6** (the second original wave being increased at the expense of the third) when small amounts of weak proton donors are added to the solution. Further addition of weak proton donors causes the second wave to shift to more positive values, because of the reversibility of the reduction of the mono-anion to the dianion. When the amount of proton donors are high enough, also the radical can be protonated to give a neutral molecule that, having a higher electron affinity than the anion radical, can be reduced to the same potential of the first wave and the polarograms of **5** and **6** show a single tetraelectronic wave.

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