Tetrahedron. Vol. 30, pp. 3741 to 3751. Pergamon Press 1974. Printed in Great Britain

ELECTROCHEMICAL AND ESR STUDIES ON THE REDUCTION OF 3-ARYLIMINO-3H-INDOLE-N,N'-DIOXIDES

R. ANDRUZZI, I. CARELLI and A. TRAZZA
Istituto Chimico della Facoltà di Ingegneria dell'Università and Centro di Elettrochimica e Chimica Fisica delle Interfasi del Consiglio Nazionale delle Ricerche, Via del Castro Laurenziano, 7-00161 Roma, Italy

and

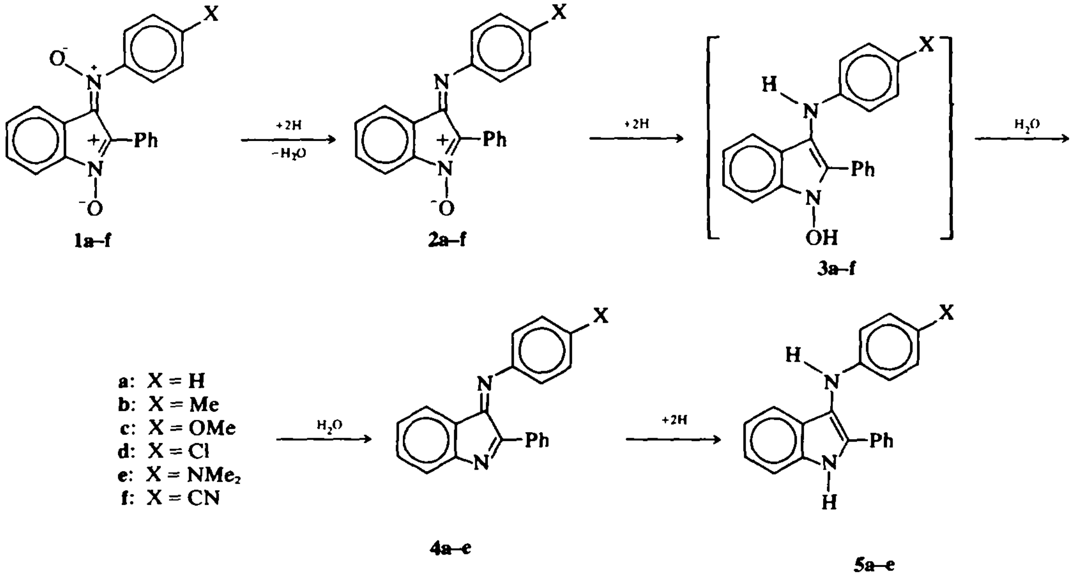
P. BRUNI and M. COLONNA*
Istituto Chimico della Facoltà di Ingegneria dell'Università—Viale Risorgimento, 2-40136 Bologna, Italy

(*Received in the UK* 1 *February* 1974; *Accepted for publication* 4 *March* 1974)

Abstract—3-Arylimino-3H-indole-N,N'-dioxides have been reduced in DMF to the corresponding radical anions, and studied using polarographic and controlled potential electrolysis, as well as UV and ESR spectrometry. A multistep scheme has been suggested in order to explain the various experimental results. ESR spectra were explained in terms of HFSC evaluation and theoretically reconstructed in order to check the validity of the attributions. The same radicals were obtained with DMSO/t-BuOK as reducing agent.

Catalytic reduction as well as the reaction with hydrazobenzene and phenylhydrazine of the title compounds were previously studied.[1] It was postulated that the reaction follows the sequence **1** to **5**.

Electrochemical reduction in DMF of 2-phenyl-3-arylimino-3H-indoles **4a–e** in the presence of protic agents[2] takes place through a single two-electron step and leads to 2-phenyl-3-arylamino-indoles **5a–e**, while the 2-phenyl-3-arylimino-3H-indole-N-oxides[3] follow a reduction process in two steps, the former of which, more positive, leads to the formation of the N-hydroxy-derivatives **3a–e**, the latter to the formation of a mixture of 1-hydroxy-2-phenyl-3-arylamino-indoles **3a–e** and of 2-phenyl-3-arylamino-indoles **5a–e**, the relative ratio depending on the



substituent in the para position in the 3-phenyl ring. (For example, ratios 80 to 20 for **3c** to **5c** and 70 to 30 for **3e** to **5e** have been observed). Recently it was demonstrated that the reduction of compound **2f** with hydrazobenzene or with molecular hydrogen leads to **3f**, that separates as a white powder from the solvent during the reaction.[4] We now report our work related to compounds **1a–f**, the reduction of which in DMF has been studied with a variety of techniques, namely polarography, controlled potential electrolysis, cyclic voltammetry as well as ESR and UV spectrometry. A Hammett correlation of the reduction potentials versus the σ_x of the parasubstituents in the 3-phenyl ring has been done and a reaction mechanism according to the experimental data has been proposed.

EXPERIMENTAL

Compounds (**1a–f**) were prepared according to reported methods.[5] N,N-Dimethylformamide (Merck, spectrophotometric grade) was purified as previously described.[6] The water content of the solvent was determined as 0·005% by Karl Fischer 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 column of molecular sieves (4A type) and then through a DMF solution containing Et_4NClO_4 and depolarizer at the same concentration as the test solution.

The polarograms were recorded with a three-electrode multifunction assembly (Amel; model 463A). The reference electrode was Hg/Hg_2Cl_2, NaCl (satd. aq.)/agar–NaCl (aq.)/agar (1·5% w/v) DMF–water (40% v/v) Et_4NClO_4 (satd.)/methyl cellulose (5% w/v)-DMF–Et_4NClO_4 (satd.)/sintered-glass disc. The half-wave potential for the reduction of cobalticinium ions in 0·1 M Et_4NClO_4/DMF solution was $E_{\frac{1}{2}} = -0{\cdot}922$ V vs. this electrode. The dropping mercury electrode (DME) with the forced separation of the drop had the following characteristics: $m = 0{\cdot}785$ mg sec^{-1}, $t = 2{\cdot}0$ sec at $h = 50{\cdot}0$ cm, $T = 25{\cdot}0$°C in DMF–Et_4NClO_4 0·1 M. A mercury pool was employed as an auxiliary electrode. Various quantities of the stock solution were added without opening the polarographic cell using a 5 ml immersion burette (0·01 ml graduation) previously described.[6] The cyclic voltammograms were recorded with a multifunction assembly (Amel; model 448) in the same cell as for the polarographic measurements. A Beckman Kemula electrode was used as a hanging mercury dropping electrode (HMDE). The controlled potential coulometry was carried out using the apparatus and the cell previously described.[6]

Chemical reductions were performed directly in the cell, under nitrogen flow, using an apparatus previously described.[7] Compounds **1a–f** were dissolved in DMSO in one arm of the cell (solution about 1×10^{-3} M), while the other arm was loaded with the corresponding amount of t-BuOK (mole ratio 1 : 1). After the deoxygenation was completed the solution was transferred into the other leg, the resulting solution shaked and forced into the flat cell. Radicals are stable enough to be studied within 30–60 min.

UV absorption 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 on a Varian E-4 ESR spectrometer, using a Varian flat cell for aqueous samples. After the electrolysis was performed the solution (about 1×10^{-3} M) was transferred under vacuum into the flat cell, the cell transferred into the ESR cavity and spectra recorded at room temperature. Experimental spectra were then simulated by means of a CDC-3600 computer system equipped with a plotter, using the HFSC reported in the text.

RESULTS

Voltammetric methods

Aprotic medium. 2 - Phenyl - 3 - arylimino - 3H - indole - N,N′ - dioxides **1a–f** were reduced in DMF (with Et_4NClO_4 as supporting electrolyte) at the DME in three (**1e**) or more (**1a–d** and **1f**) subsequent steps (Fig 1). Half-wave potentials ($E_{1/2}$) and polarographic data are reported in Table 1, together with polarographic data registered under the same experimental conditions of the reduction steps for mono-N-oxides **2a–f** and for 3 - arylimino - 3H - indoles **4a–e**. The limiting currents of every reduction step are proportional to the concentration of the dioxides **1a–f**, in the examined range (1×10^{-4} – 1×10^{-3} M). All the di-N-oxides **1a–f** exhibit the same cyclic voltammetric behaviour at a hanging mercury drop electrode, in Et_4NClO_4–DMF solution. Typical cases are those of 2 - phenyl - 3 - (p - dimethylamino)phenylimino - 3H - indole - N,N′ -

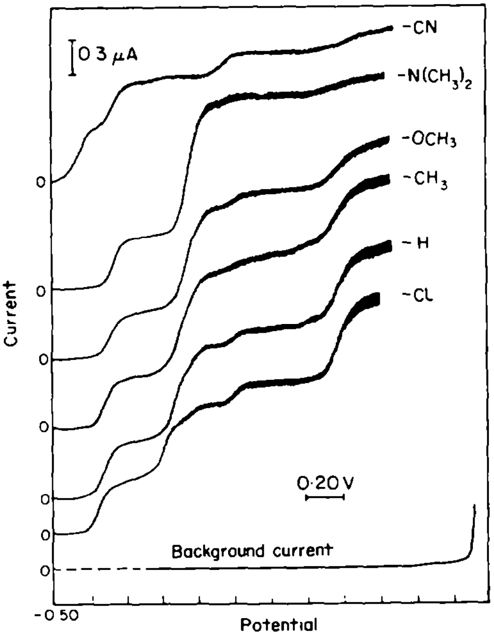
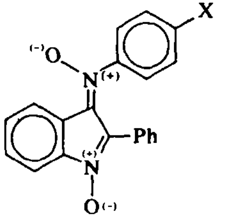
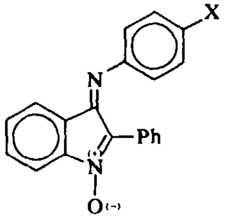
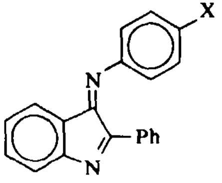


Fig 1. Polarograms of 2 - phenyl - 3 - aryl - imino - 3H - indoles - N,N′ - dioxides **1a–f** in DMF-Et_4NClO_4 0·1 M (The experimental conditions are reported in Table 1).

Table 1. Polarographic data for the reduction of N,N'-dioxides **1a–f**, mono N-oxides **2a–f** and 3-arylimino-3H-indoles **3a–e**[a]

X	σ_X[b]	 **1a–f**										 **2a–f**						 **3a–e**					
		$-E^{I}_{1/2}$ (V)	i_d^{I} (μA)	Slope[c] (mV)	$-E^{II}_{1/2}$ (V)	i_d^{II} (μA)	$-E^{III}_{1/2}$ (V)	i_d^{III} (μA)	$-E^{IV}_{1/2}$ (V)	i_d^{IV} (μA)	$-E^{I}_{1/2}$ (V)	i_d^{I} (μA)	$E^{II}_{1/2}$ (V)	i_d^{II} (μA)	$-E^{III}_{1/2}$ (V)	i_d^{III} (μA)	$-E^{I}_{1/2}$ (V)	i_d^{I} (μA)	$-E^{II}_{1/2}$ (V)	i_d^{II} (μA)	$-E^{III}_{1/2}$ (V)	i_d^{III} (μA)
—H	0·00	0·780	0 46	65	1 221	0·85	1 521	0 13	2·081	0·67	0·955	0·44	1·294	0·43			0·944	0·48	1·248	0·25	2·277	0·28
—CH_3	−0·17	0·805	0·45	63	1·229	0·89	1·565	0·14	2·117	0·61	0·984	0 47	1·299	0 47	2·214	0·06	0 980	0 44	1·291	0·25	2·269	0·24
—OCH_3	−0·27	0·827	0 41	63	1 257	0·88	1·292	0 12	2·097	0·40	0·996	0·49	1·291	0·42	2·187	0·08	0·986	0·49	1 331	0·29	2 265	0·26
—Cl	0·23	0·750	0·43	59	1 119	0·69	1·813	0·18	2·081	0·71	0·917	0·46	1·244	0·40	2·123	0·06	0·915	0·48	1·193	0·24	2·250	0·31
—$N(CH_3)_2$	−1·05 to −0·21	0·859	0·45	57	1·253	1·18			2·085	0·13	1·035	0·50	1·342	0·44	2·309	0·08	1·034	0·47	1·350	0·36	2·214	0·12
—CN	0·66	0·674	0·46	69	0·874	0·43	1·486	0·20	2·164	0·17	0·860	0·48	1·097	0·43	2·012	0·06						

[a] Solutions in DMF–Et_4NClO_4 0·1 M with about 3×10^{-4} M depolarizer; h = 50·0 cm; T = 25·0°C.

[b] Substituent constants, from P. Zuman, *Substituent effects in Organic Polarography*, Plenum Press, N.Y., 1967, Chap. III.

[c] Slope was calcd. using $E_{1/4}$–$E_{3/4}$ values, which equals 56/n mV for a reversible process and $56/\alpha n_a$ mV for an irreversible process.

dioxide **1e** and of 2 - phenyl - 3 - (p - cyano) phenylimino - 3H - indole - N,N' - dioxide **1f** that are reported in Fig 2. As can be seen in Fig 2b with potential span restricted to that of the first polarographic plateau, the first cathodic step has a clear corresponding anodic peak. Moreover, in the range of the used scan rate ($v = 0{\cdot}10$–$1{\cdot}00\ V\ sec^{-1}$) peak potentials are essentially independent from the scan rate. The separation between anodic and cathodic peak potentials is close to the theoretical value[8] for a reversible one-electron transfer. The ratio anodic (ip_a) to cathodic (ip_c) peak currents is close to unity and the current function ($ip_c/v^{1/2}$) does not change with varying scan rate.

Protic medium. Reduction in the presence of protonating agents has been studied in order to elucidate a possible reaction mechanism. When increasing amounts of 2,4-dimethylphenol ($pK_a > 15$) were added to the solution of di-N-oxides **1a–f** in DMF–Et_4NClO_4 0·1 M, two different behaviours were observed: in the case of compounds **1a–c** and **1e**, using a molar ratio $O < r < 4$, between the protonating agent and the di-N-oxide, the potentials corresponding to the first and to the second polarographic wave shift to more positive values. In addition a new wave appears between the first and the second wave found in aprotic medium; this new wave increases causing the second one to decrease. In the same way the third wave found in aprotic experiments increases causing the fourth to decrease. With $r \gg 4$ the polarogram shows a single wave the height of which is almost four times the first wave found in aprotic medium. Moreover, the rising part of the single wave interests a wide potential span and its height increases by adding an authentic sample of the corresponding mono-N-oxide (**2a–c** or **2e**).

Fig 3 shows a typical behaviour corresponding to compound **1e**. Polarograms of compounds **1d** or **1f**, on the contrary (Fig 4), show an increase of the first wave at the expense of the second one, both potentials shifting to more positive values, when a molar ratio $O < r < 1$ between protonating agent and di-N-oxide is used; at the same time third

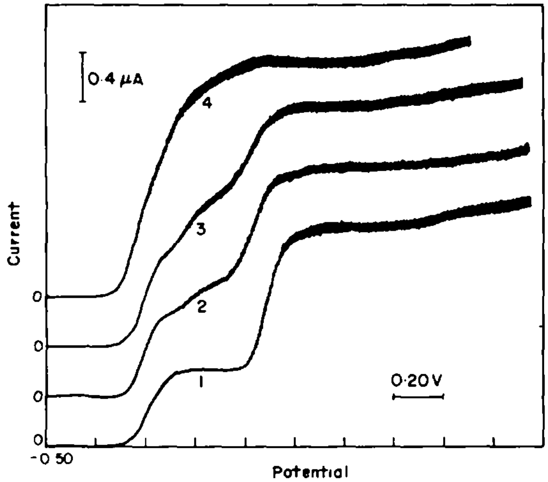


Fig 3. Effect of increase mole ratio 3,4 - dimethylphenol/N,N' - dioxide **1e**, r, on the polarogram of $3{\cdot}05 \times 10^{-4}$ M **1e** in DMF-Et_4NClO_4 0·1 M. r: (1), 0; (2), 1·46; (3), 3·24; (4), 19·47. (tg = 2·0 sec; h = 50·0 cm; T = 25·0°C).

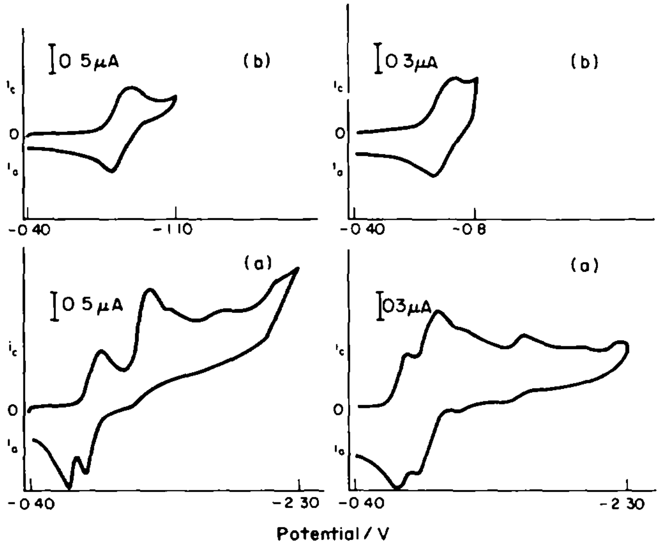


Fig 2. Cyclic voltammograms of about $2{\cdot}3 \times 10^{-4}$ M N,N'-dioxide **1e** (on the left) and N,N'-dioxide **1f** (on the right) in DMF-Et_4NClO_4 0·1 M. (a) Potential span including all polarographic waves; (b) potential span restricted to that of the first wave. (Scan rate 1·00 V × sec^{-1}; hanging drop = 1·0 μl; T = 25°C).

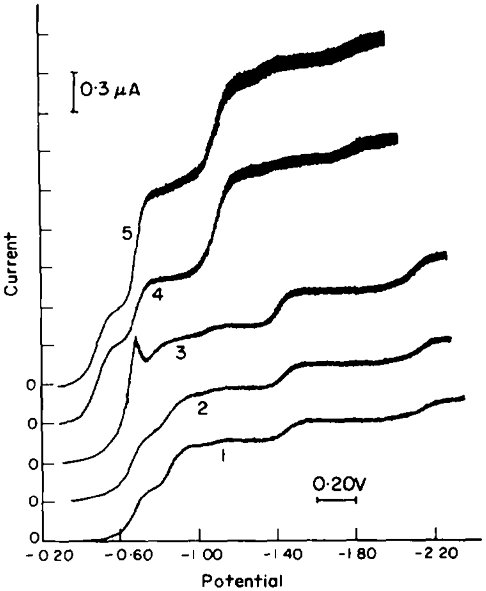


Fig 4. Effect of increase mole ratio 3,4 - dimethylphenol/N,N' - dioxide **1f**, r, on the polarogram of $3{\cdot}18 \times 10^{-4}$ M **1f** in DMF-Et_4NClO_4 0·1 M. r: (1), 0; (2), 0·3; (3), 1·1; (4), 12·28; (5) as (4) with mono N-oxide **2f** $1{\cdot}8 \times 10^{-4}$ M.

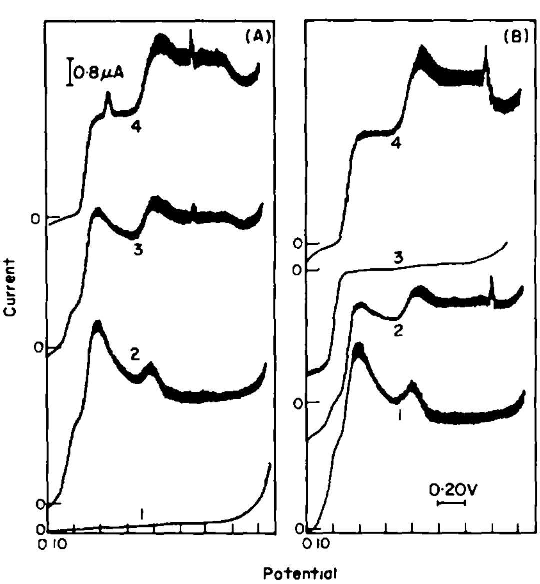


Fig 5. Polarograms of N,N'-dioxide **1d** during various stages of coulometric reduction and oxidation at a mercury pool electrode. (h = 80·0 cm; T = 22·0°C). (A) (1) Background current of DMF-Et_4NClO_4 0·1 M with $CH_2ClCOOH$ $4{\cdot}5 \times 10^{-2}$ M; (2) in the presence of N,N'-dioxide **1d** $5{\cdot}0 \times 10^{-4}$ M ($2{\cdot}2 \times 10^{-5}$ mol); (3) soln in (2) partially reduced at $-0{\cdot}12$ V (number of coulombs passed Q = 2·1); (4) soln in (2) completely reduced at $-0{\cdot}12$ V (Q = 4·2). (B) (1) $5{\cdot}0 \times 10^{-4}$ M ($2{\cdot}2 \times 10^{-5}$ mol) N,N'-dioxide **1d** in DMF-Et_4NClO_4 0·1 M with $CH_2ClCOOH$ $4{\cdot}5 \times 10^{-2}$ M; (2) soln in (2) partially reduced at $-0{\cdot}45$ V (Q = 4·1); (3) soln in (2) completely reduced at $-0{\cdot}45$ V (Q = 8·5); (4) soln in (3) completely oxidized at $-0{\cdot}05$ V (Q = 4·2). The capillary constants of the DME under a mercury head of 80·0 cm at 22·0°C in soln (4) were m = 1·73 mg sec^{-1}, t = 3·70 sec at E = $-0{\cdot}50$ V.

and fourth wave increase. For ratios $r > 1$ the polarograms exhibit maxima [Fig 4 polarogram (3)], nevertheless with $r > 12$, they show three waves the total height of which is more than four times the value found for the first wave in aprotic medium; adding known amounts of the corresponding mono-N-oxides **2d** or **2f** only the second polarographic wave increases: in Fig 4 the characteristic behaviour of **1f** is reported. When monochloroacetic acid ($pK_d \simeq 10$) or benzoic acid ($pK_d \simeq 12$) were used as stronger protonating agents, the polarogram of all compounds **1a–f** shows another reduction wave at more positive potentials. For ratios between acid and substrate higher than 1 the polarograms exhibit maxima and drop-time irregularities. Nevertheless, for $r > 50$ it is possible to see on the polarogram two reduction steps badly separated (see as an example polarogram 1 in Fig 5B); on the contrary, no separation was observed in the case of **1e**. In any case the height of the first wave doubles the value of the first wave found in aprotic medium and the unique wave for **1e** is about four times the corresponding first wave found in the aprotic medium.

Controlled potential coulometry and spectroscopy

Protic medium. Coulometric determinations on all compounds of the series **1a–f** in Et_4NClO_4–DMF with different amounts of monochloroacetic acid ($10 < r < 100$) were made at the potential ($-0{\cdot}50$ V) corresponding to the plateau of the single (compound **1e**) or of the second (**1a–d** and **1f**) polarographic wave. The number of faradays per mole involved in the reduction was found to be $n_{app} = 4{\cdot}0 \pm 0{\cdot}1$. After reduction, UV absorption spectra of the colourless solutions (λ_{max} = 306–308 nm; ϵ = 17·000 l mol^{-1} cm^{-1}) were found identical to the ones obtained from the electrochemical reduction ($n_{app} = 2{\cdot}0$) of the mono N–oxides **2a–e**, that were previously assigned to the corresponding 1-hydroxy derivatives **3a–e**.[3] Reversal coulometry at $-0{\cdot}05$ V (oxidation) involved two electrons per molecule of depolarizer; the spectral absorption curve (λ_{max} = 281–288 nm; $\epsilon = 29 \div 35{\cdot}000$ l mol^{-1} cm^{-1}) and the polarogram were identical to the ones shown by mono N–oxides **2a–e**.[3] Moreover, the same UV spectra and polarograms attributed to the mono N–oxides were obtained after reduction at the potentials of the first polarographic wave ($n_{ap} = 2{\cdot}0 \pm 0{\cdot}1$) of the di-N-oxides **1a–f**. Fig 5 shows the polarograms of 2 - phenyl - 3 - (p - Cl - phenyl -) imino - 3H - indole - N,N' - di - oxide **1d** at various stages of reduction and oxidation.

Aprotic medium. The coulometric determinations of **1a–f** in DMF–Et_4NClO_4 at potentials corresponding to the plateau of first polarographic wave gave values of n_{app} ranging from 1·2 to 2·5 faradays per mole and the electrolysis current decayed to a value higher than that of the corresponding background currents. The polarograms recorded during the electrolysis showed either a progressive decrease in first, second and fourth wave or an increase in the third wave. Nevertheless, as the reduction proceeds also this last wave decreases, so that the polarogram shows none of the original reduction waves. Solutions of **1a–f** reduced using approximately one electron per mole of depolarizer showed a deep green colour and gave intense ESR signals, that are reported in figure 6, 7 and 8; Table 2 shows the hyperfine splitting constants for anion radicals $[\mathbf{1a–f}]^{\dot{-}}$.

The chemical reduction in DMSO/t-BuOK ($MeSOCH_2^-$ being the reducing agent[7]) led to the same signals, though a worse resolution of the spectra has been observed in all the cases we studied. The fact can demonstrate that there is no appreciable effect on the radical by the solvent, nor there is by Et_4NClO_4, as far as the solvents in question are concerned.

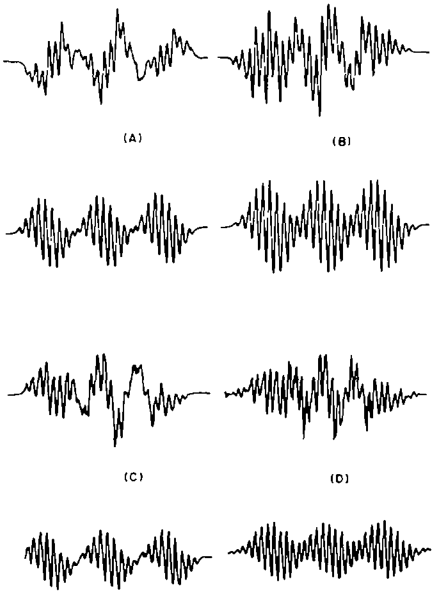


Fig 6. Experimental (top) and simulated (bottom) ESR spectra attributed to 2 - phenyl - 3 - (p - methoxy-) phenylimino - 3H - indole - N,N' - dioxide anion radical (A); 2 - phenyl - 3 - phenylimino - 3H - indole - N,N' - dioxide anion radical (B); 2 - phenyl - 3 - (p - chloro) phenylimino - 3H - indole - N,N' - dioxide anion radical (C); 2 - phenyl - 3 - (p - methyl-)phenylimino - 3H - indole - N,N' - dioxide anion radical (D).

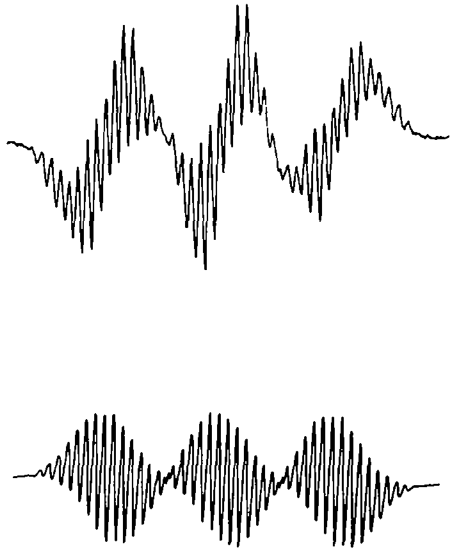


Fig 7. Experimental (top) and simulated (bottom) ESR spectra attributed to 2 - phenyl - 3 - (p - dimethylamino-)phenylimino - 3H - indole - N,N' - dioxide anion radical.

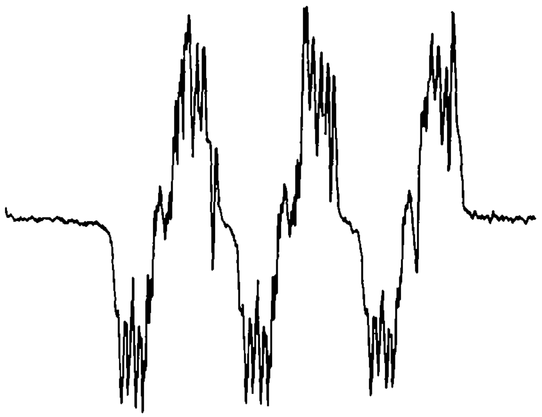
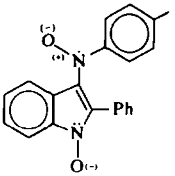
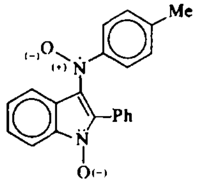
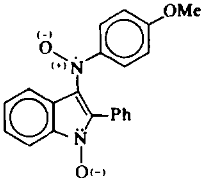
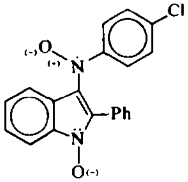
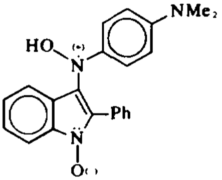
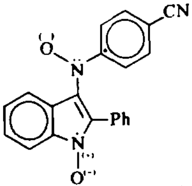
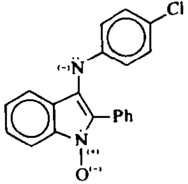
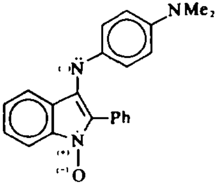


Fig 8. Experimental ESR spectrum attributed to 2 - phenyl - 3 - (p - cyano-)phenylimino - 3H - indole - N,N'- dioxide anion radical.

The controlled potential electrolysis performed at the potentials of the second or third polarographic wave plateau involved values of n_{app} ranging from 2·2 to 3·2 faradays per mole of **1a–d** and **1f** and of n_{app} equal to 4 faradays for **1e**. When the solutions obtained by reduction using about 2·5 electrons per mole were transferred into the spectrometer cavity, new spectra were registered (see Fig 9) that call for nitroxides of a new type and to which structures $[\mathbf{2a–e}]^{\dot{}}$ have been attributed (see following discussion). We must notice that all the radicals reported show the presence of impurities of some extent, due perhaps to secondary reactions that led the reduction to be not stoichiometric. Finally, the coulometric determination made at the fourth polarographic wave potentials involved more than four faradays per mole and the elec-

Table 2. Hyperfine splitting constants for anion radicals

Starting compound	HFSC	Signal attributed to radical:
1a	$a^N_{exo} = 9{\cdot}25$; $a^N_{endo} = 1{\cdot}10$ g $a^H_{o,p} = 2{\cdot}40$ g; $a_m{}^H = 1{\cdot}20$ g	
1b	$a^N_{exo} = 10{\cdot}75$ g; $a^N_{endo} = 1{\cdot}10$ g $a_o{}^H = a^H_{Me} = 2{\cdot}50$ g $a_m{}^H = 1{\cdot}10$ g	
1c	$a^N_{exo} = 9{\cdot}75$ g; $a^N_{endo} = 1{\cdot}10$ g $a_o{}^H = 2{\cdot}25$ g; $a_m{}^H = 1{\cdot}10$ g	
1d	$a^N_{exo} = 10{\cdot}05$ g; $a^N_{endo} = 1{\cdot}00$ g $a_o{}^H = 2{\cdot}25$ g; $a_m{}^H = 1{\cdot}00$ g	
1e	$a^N_{exo} = 10{\cdot}05$ g; $a_o{}^H = a^H_{OH} = 2{\cdot}40$ g $a_m{}^H = a^N_{NMe_2} = a^H_{NMe_2} = 0{\cdot}80$ g	
1f	$a^N_{endo} = 5{\cdot}90$ g	
2d	$a^N_{endo} = 5{\cdot}82$ g	
2e	$a^N_{endo} = 5{\cdot}88$ g	

trolysis current decayed to a value higher than that of the corresponding background currents.

When the reduction was carried out using about 3·5 electrons per mole of depolarizer a new radical was observed (see Fig 10) the nature of which has not yet been investigated; in any case it is important to notice that the same ESR spectrum was obtained in the mono-electronic reduction of 2 - phenyl - 3 - imino - 3H - indole[9] and of 2 - phenyl - 3 - oxo - 3H - indole.[9]

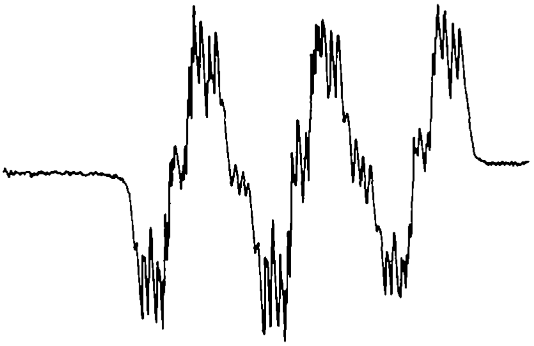


Fig 9. Experimental ESR spectrum attributed to 2 - phenyl - 3 - (p - chloro-)phenylimino - 3H - indole - N - oxide anion radical.

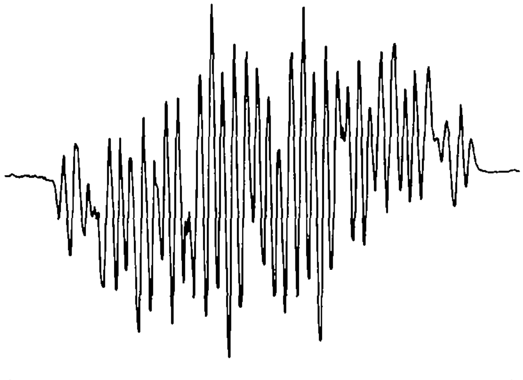


Fig 10. ESR spectrum obtained in the reduction with more than three electrons per mole of **1a–d**.

DISCUSSION

The results of polarographic, coulometric and spectrometric measurements suggest that in DMF–Et_4NClO_4 and in the presence of proton donors like monochloroacetic acid, compounds **1a–d** and **1f** can be reduced to the corresponding mono-N-oxides **2a–d** and **2f**, two electrons per mole of depolarizer being involved. In the case of **1e**, on the contrary, the reduction process involves four electrons and produces N-hydroxy derivative **3e**. The subsequent oxidation of the latter compound uses up two electrons and the corresponding mono-N-oxide **2e** is formed.

In aprotic medium the reduction process begins at the DME with a reversible mono-electronic step, leading to the formation of the anion radicals [**1a–f**]$^{\cdot-}$, proved by ESR. Comparing the half-wave potentials of the first polarographic step (Table 1) the electron affinity changes as the para substituent X in 3-phenyl ring changes, following the expected order

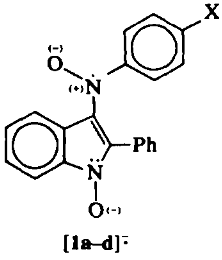
$$CN > Cl > H > Me > OMe > NMe_2$$

and according to the simple modified form of Hammett's equation[10]

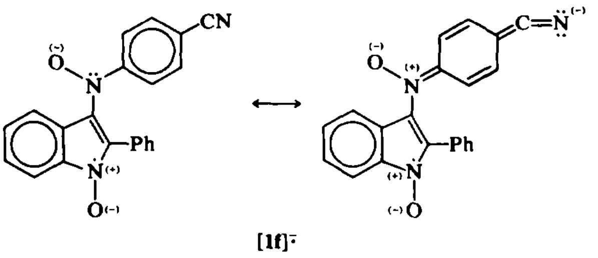
$$\Delta E_{1/2} = \gamma_{\pi,R}\sigma_X$$

where $\Delta E_{1/2}$ is the substituent shift of half-wave potentials: $(E^1_{1/2})_X - (E^1_{1/2})_H$; σ_X is the substituent constant (Table 1) and $\gamma_{\pi,R}$ the reaction constant, which equals 0·16 V.

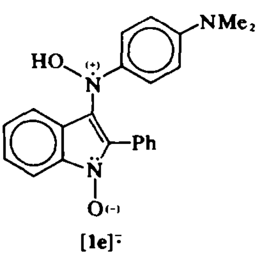
This correlation clearly shows that the full series of compounds **1a–f** follows the same initial reaction mechanism (relative to the first electron consumed). Three different kinds of ESR spectra were obtained; they have been interpreted in terms of a structure bearing either an esocyclic nitroxide group [**1a–d**]$^{\cdot-}$, or an endocyclic nitroxide group [**1f**]$^{\cdot-}$, while [**1e**]$^{\cdot-}$ has been interpreted in terms of the protonated exocyclic nitroxide. As a matter of fact, Table 2 and Figs 6, 7 and 8 show that the nitrogen HFSC has value of about 9–11 gauss for **1a–e** while it has a value of 5·90 gauss in the case of **1f**. Literature[11,12] reports a_N values of about 10 gauss for aliphatic nitroxides and values of 4–6 gauss for nitroxides where nitrogen resides in an aromatic ring. The fact that in [**1f**]$^{\cdot-}$ the unpaired electron resides preferably on the endocyclic nitrogen can be explained on the basis of a resonance stabilisation.[13] Spectrum in Fig 8 should be attributed also to anion radical [**2f**]$^{\cdot-}$. The fact that we propose structure [**1f**]$^{\cdot-}$ depends on two kinds of observations: on the one hand reduction of the more basic **1e** leads to



[**1a–d**]$^{\cdot-}$



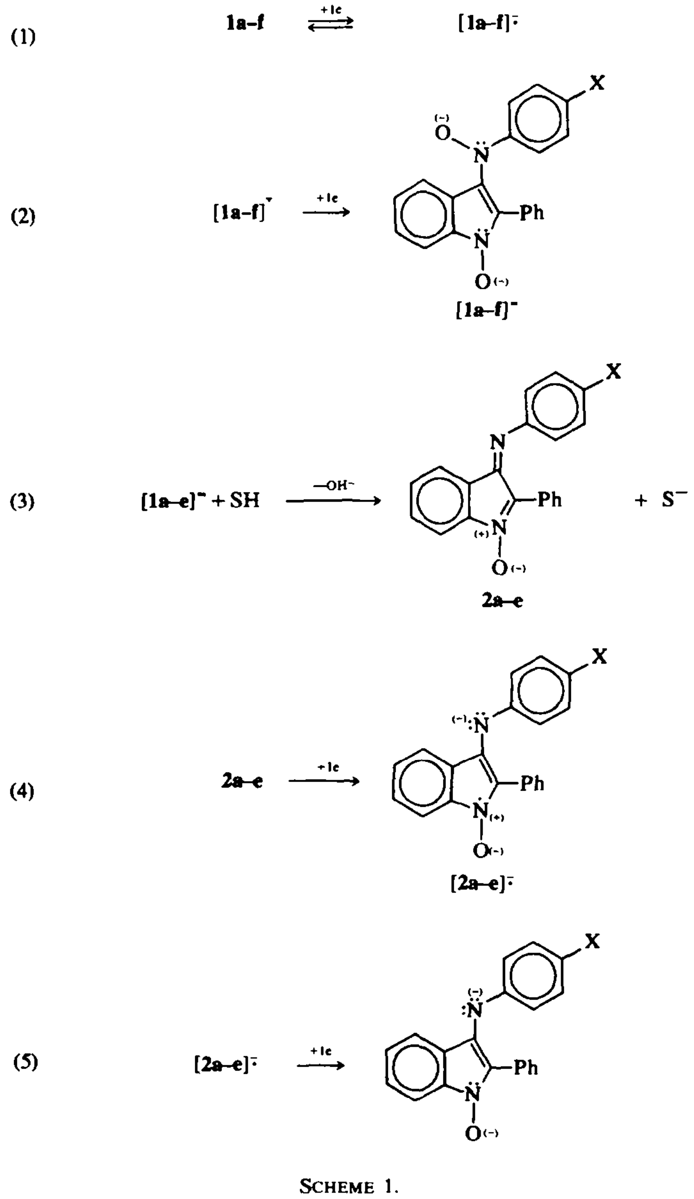
[**1f**]$^{\cdot-}$



[**1e**]$^{\cdot-}$

the di-N-oxide anion radical, on the other less than one electron per mole was used up to produce the radical in question. These considerations lead us to believe that either radical [**1f**]$^{\overline{\cdot}}$ alone or a mixture of [**1f**]$^{\overline{\cdot}}$ and [**2f**]$^{\overline{\cdot}}$ are present. Further support to this idea can be found in the following discussion on the polarographic behaviour of **1f**.

The first reduction step is followed by a second one that is monoelectronic in the case of [**1f**]$^{\overline{\cdot}}$, almost trielectronic in the case of [**1e**]$^{\overline{\cdot}}$ and shows values included between 1 and 3 for the other radicals. On the basis of these results we propose the following scheme: where SH behaves as a protonic source present in DMF (such as traces of water, DMF, etc.). As the polarographic data (Table 1) show, the potential involved in reaction (4) is less negative than that involved in reaction (2). Moreover, the scheme shows that the reduction of radical [**1a–f**]$^{\overline{\cdot}}$ (reaction 2) can go on (reactions 4 and 5), and ascribes a determining function to the protonation of the corresponding dianion followed by elimination of OH^- (reaction 3). In the case of compound **1f** the different behaviour with respect to all the other compounds must depend on a smaller disposition of dianion [**1f**]$^{=}$ to both reactions (step 3) so that its



Scheme 1.

polarogram (Fig 1) shows two-monoelectronic waves. The strong electron-withdrawing effect of –C≡N, (certainly much higher than that of the other groups, as the σ_X values reported in Table 1 show) reduces the amount of negative charge on group >N–O, so reducing its aptitude to protonation; on the other hand if we assume that partial protonation can occur, –C≡N opposes OH^- elimination.

The proposed anomalous behaviour of **1e**, that leads to a neutral radical, can be explained in terms of high basicity of the corresponding radical that allows it to extract a proton from any source (SH) present in the reaction mixture: this hydrogen atom should be bonded either to the NMe_2 group or to the >N—O group. A better fit between experimental and simulated spectra has been obtained using the structure bearing the >N—OH group: the ratio $a^{N}_{NOH}/a^{H}_{NOH} = 4{\cdot}2$ is in good agreement with values previously reported.[14]

The higher proton affinity of radical [**1e**]$^{\overline{\cdot}}$ can justify the fact that the second wave is a quesi-trielectronic step (Fig 1). The potential necessary for reaction (4) to take place results more negative (about 100 mV) than that necessary for reaction (2). On the contrary, if we consider that the reduction of [**2e**]$^{\overline{\cdot}}$ could involve a protonated form, the potential necessary to reaction (5) should be less negative. In all the other cases the reduction can proceed following path (4) with formation of [**2a–d**]$^{\overline{\cdot}}$ so that the corresponding polarograms (Fig 1) show a second quasi bielectronic reduction step.

The higher disposition of the reaction medium to leave protons (case of o-xylenol) makes all the di-N-oxide anion radicals be immediately protonated, and gives a species that is in fact a neutral radical. This radical shows a higher electron affinity with respect to the anion radical and consequently can be reduced at the potentials of the first polarographic wave (which in this way becomes bielectronic) so that the corresponding mono-anions [**1a–f**]H^- are formed. A similar mechanism has been proposed for the polarographic reduction of conjugated hydrocarbons in solvents with limited proton availability.[15] Anions [**1a–f**]H^-, then can easily be transformed into the corresponding mono N-oxides **2a–f**, that in the presence of o-xylenol, are reduced at the same potentials as **1a–c** or **1e** (Fig 3) or at more negative potentials than **1d** or **1f** (Fig 4) to the corresponding neutral radicals which in turn are reduced to the corresponding anions. Support for this statement can be found in the fact that when an amount of the corresponding mono-N-oxide is added to the solution of the dioxide, in DMF and o-xylenol, the polarogram shows an increase of the single wave in the case of **1a–c** and **1e**, or of the second wave in the other cases [see Fig 4, polarogram (5)].

The time necessary for electrolysis allows the protonation of radical [**1a–f**]$^{\overline{\cdot}}$ and the consequent reactions also in aprotic medium (protonic source being SH), so that a greater number of faradays per mole of depolarizer is involved when the coulometric determination is performed at the potentials either of the first monoelectronic polarographic wave or of the second quasi bielectronic wave.

The presence of a stronger protonating agent such as monochloroacetic acid or benzoic acid, in addition to the effect reported for the o-xylenol, affects the potential of step (1) in Scheme 1 because the electron transfer at the electrode can be preceded and/or be simultaneous with a fast protonation reaction, which makes the free energy change involved in the reduction process lower, so that the polarogram shows a new tetra-electronic wave (compound **1e**) or two bi-electronic waves (compounds **1a–d** and **1f**) all at less negative potentials (Fig 5).

When the reduction is carried out at potentials corresponding either to the second or to the third polarographic step and in aprotic medium a new radical species appears, that requires about three electrons. The attribution of its structure can be easily made following considerations reported on the first part of this discussion. An HFSC of about 5·8–5·9 gauss for one nitrogen nucleus has been found, which is in accord with values reported for aromatic N-oxide radicals.[11,12] Some further hyperfine structure that cannot be attributed for lack of appropriate derivatives is present. In addition it must be noticed that all the mono N-oxide anion radical spectra show extralines due to some impurities. From the polarographic data reported in Table 1 it can be seen that the height of the third polarographic wave completes almost the second wave height, so as to have a total three electron process; obviously this cannot be said for **1f**.

As regards the reduction process related to the fourth polarographic wave, nothing can be reasonably said. As Table 1 shows, this wave appears at a high negative potential, that is about the same observed at the third polarographic wave in the reduction of 2 - phenyl - 3 - arylimino - 3H - indoles **3a–e**; in addition no effect of the para substituent in the 3-phenyl group has been observed.

It is reasonable to suppose that the process related to the higher potential can involve a cleavage of the molecule. This assumption is supported by the observation of a new radical that shows an ESR spectrum identical to that obtained by analogous reductions of 3-oxindole and 3 - imino - 3H - indole, which clearly demonstrates that the group in position 3- cannot be involved in the spectrum hyperfine structure. Work is in progress in order to elucidat the nature of this radical and to investigate the mechanism involved in the fourth wave process.

REFERENCES

[1] M. Colonna and P. Bruni, *Boll. Sci. Fac. Chim. Ind. Bologna* **25**, 41 (1967)

[2] R. Andruzzi, M. E. Cardinali, I. Carelli and A. Trazza, *J. Electroanal. Chem.* **36**, 147 (1972)

[3] R. Andruzzi, M. E. Cardinali and A. Trazza, *Ibid.* **41**, 67 (1973)

[4] M. Colonna, L. Greci and M. Poloni, unpublished results

[5] M. Colonna and P. Bruni, *Gazz. Chim. Ital.* **95**, 1172 (1965); *Ibid.* **97**, 1569 (1967)

[6] R. Andruzzi, M. E. Cardinali, I. Carelli and A. Trazza, *J. Electroanal. Chem.* **26**, 211 (1970)

[7] G. A. Russell, E. T. Strom and E. G. Janzen, *J. Am. Chem. Soc.* **86**, 1807 (1964)

[8] R. S. Nicholson and I. Shain, *Anal. Chem.* **36**, 706 (1964)

[9] P. Bruni and A. Trazza, unpublished results

[10] P. Zuman, *Substituent Effects in Organic Polarography*, Plenum Press, N.Y., 1967, Chap. VIII

[11] P. Bruni and M. Colonna, *Tetrahedron* **29**, 2425 (1973)

[12] R. Ramasseual and A. Rassat, *Bull. Soc. Chim. Fr* 4330 (1970)

[13] R. I. Walter *et al.*, *J. Phys. Chem.* **71**, 2290 (1967); *J. Am. Chem. Soc.* **88**, 1923 (1966)

[14] B. M. Hoffman and T. B. Eames, *Ibid.* **91**, 2169 (1969)

[15] G. J. Hoijtink, J. Van Scooten, E. De Boer and W. Y. Aalbersberg, *Rec. Trav. Chim.* **73**, 355 (1954)