Electrochemical Investigations on Nitro-substituted Hydrazono Compounds

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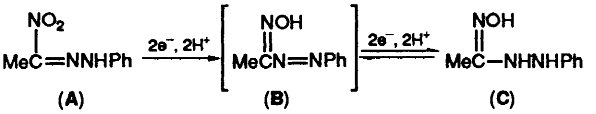
The electrochemical reduction of 3-(*N*-nitro-*N*-phenylhydrazono)pentane-2,4-diones has been studied over a wide pH range at dropping mercury and glassy carbon electrodes. These compounds give two four-electron waves corresponding to the reduction of nitro and hydrazono groups, and one two-electron waye corresponding to the C–N reductive bond. On the basis of polarography, linear and cyclic sweep voltammetry, coulometry, IR, mass, and ^{1}H NMR spectral studies, and product identification, a reaction mechanism is suggested to account for the reduction mechanism.

The polarographic behaviour of hydrazono compounds has been the subject of many investigations.[1–7] The reduction of hydrazones has been reviewed in detail by Turtan.[8] Fundamental contributions in this field have been made by Kitaev *et al.*[9–13] and by Lund.[1,14] The mechanism of the reduction has been discussed in Kitaev and Buzykin's review.[15] A four-electron reduction is usually observed in acidic solutions,[10–14] involving the cleavage of the -N-N- bond during the reduction. More recently, four-electron reduction of the hydrazones has been reported[16–18] in acidic as well as in alkaline media with the formation of amino compounds. On the other hand Zuhri and Shalebi[4] have found a two-electron reduction followed by hydrolysis resulting in the formation of the corresponding carbonyl compounds. Hydrolysis of the reduced product has also been observed by Lund[3] for similar hydrazones. However, Fahmy *et al.*[19] have reported further reduction of the amino compound, formed after four-electron reduction, to ammonia and ketone in a two-electron wave.

Several reviews[20–22] have appeared in the literature on the electro-reduction of nitro compounds. Many reports are available on the electrochemical reduction of nitro compounds in pure aqueous,[23,24] mixed aqueous–organic,[23,25,26] and non-aqueous solvents.[27–30] Protonated *N*-nitramines are reduced in a single six-electron wave to the unsymmetric hydrazine[31–34] together with some amine[34] in acidic solutions, whereas *N*-nitrosamines are reducible in both acidic and alkaline solutions. The protonated compound is reduced in a four-electron reaction resulting in the formation of hydrazine, whereas the unprotonated nitrosamine consumes only 2 electrons.[35–38] The only polarographic study dealing with nitro hydrazones shows[39] that the phenylhydrazone of nitroacetaldehyde, compound (**A**), yields, at all pH values examined, a single polarographic wave corresponding to a four-electron reduction [equation (1)]. The presence of hydrazo oxime (**C**) was confirmed based on its two-electron anodic wave, corresponding to an oxidation yielding the azo-oxime (**B**).



$$\underset{(\mathbf{A})}{\mathrm{Me}\overset{\overset{NO_2}{|}}{C}{=}NNHPh} \xrightarrow{2e^-,\,2H^+} \left[\underset{(\mathbf{B})}{\mathrm{Me}\overset{\overset{NOH}{||}}{C}N{=}NPh}\right] \underset{}{\overset{2e^-,\,2H^+}{\rightleftharpoons}} \underset{(\mathbf{C})}{\mathrm{Me}\overset{\overset{NOH}{||}}{C}{-}NHNHPh} \qquad (1)$$

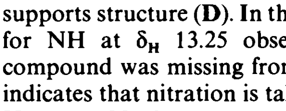
No reference has been found dealing with compounds bearing a nitro group on the nitrogen atom of a hydrazono group ($\overset{\overset{NO_2}{|}}{-N}-N{=}C<$). In this paper, the electrochemical behaviour of 3-(*N*-nitro-*N*-phenylhydrazono)pentane-2,4-diones has been investigated to throw some light on the reduction mechanism.

Experimental

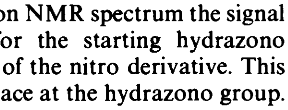
Various compounds listed in Table 1 were synthesized and characterized in the following manner.

3-(Phenylhydrazono)pentane-2,4-dione (0.02 mol) was added to a constantly stirred suspension of acetic anhydride (25 cm^3) and nitric acid (20 cm^3). The reaction was carried out at 25 °C. After reaction, the mixture was kept at room temperature for 30 min and then poured over crushed ice (250 g). The precipitate so obtained was filtered off, thoroughly washed with water, and dried. The *product* was recrystallized by dimethylformamide (DMF) as yellow crystals, m.p. 128 °C (Found: C, 53.2; H, 4.25; N, 16.5. $C_{11}H_{11}N_3O_4$ requires C, 53.01; H, 4.41; N, 16.86%); ν_{max}(KBr) 1 670vs, 1 590s, 1 323s, 850vs, and 750s cm^{-1}; δ_H[270 MHz; $(CD_3)_2SO$] 7.4 (5 H, Ph) and 2.4 (6 H, s, 2 Me); *m/z* 249 (M^+).

Other *N*-nitro compounds of this series were similarly synthesized and their m.p.s are compiled in Table 1. The nitro products obtained by this method may have the structure (**D**) or (**E**).



(D)

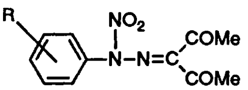


(E)

Spectral and electrochemical studies indicate that the synthesized compounds have the hydrazono group (**D**) rather than structure (**E**) bearing an azo group. In the IR spectrum a strong band at 1 590 cm^{-1} can be assigned to >C=N and supports structure (**D**). In the proton NMR spectrum the signal for NH at δ_H 13.25 observed for the starting hydrazono compound was missing from that of the nitro derivative. This indicates that nitration is taking place at the hydrazono group. However, NMR spectra cannot rule out the possibility of the existence of structure (**E**), in which the NH group is also absent. Confirmatory evidence for structure (**D**) was obtained from electrochemical studies. Azo compounds are usually reduced to the hydrazo form in a two-electron step[39–41] or, if an OH or NH_2 group is present in an *ortho* or *para* position, to aniline in a four-electron step. Aryl hydrazones[1–3] are reduced in a four-electron step involving cleavage of the N–N bond. Controlled-potential electrolysis of the studied compound at −1.8 V in acidic media (pH 2.0 and 4.0) resulted in a 10-electron process yielding phenylhydrazine following reactions (2)–(4).

$$ArN(NO_2)N{=}CR_2 + 4e^- + 4H^+ \longrightarrow ArN(NHOH)N{=}CR_2 + H_2O \qquad (2)$$

Table 1. Polarographic characteristics of 3-(*N*-nitro-*N*-arylhydrazono)pentane-2,4-diones at pH 8.5 in (35% DMF).[a]



R	M.p./°C	$-(E_{\frac{1}{2}})_1$/V	$-(E_{\frac{1}{2}})_2$/V	$-(E_{\frac{1}{2}})_3$/V	$(i_d)_1$/μA	$(i_d)_2$/μA	$(i_d)_3$/μA
H	128	0.44	0.67	1.50	0.20	0.20	0.10
2-OMe	142	0.45	0.68	1.52	0.25	0.20	0.12
4-OMe	175	0.45	0.65	1.52	0.20	0.20	0.10
2-Cl	140	0.45	0.67	1.50	1.20	0.20	0.12
3-Cl	158	0.45	0.67	1.50	1.20	0.25	0.11
2-CO_2H	201	0.48	0.65	1.53	0.25	0.20	0.12
4-Cl, 2-NO_2	120	0.46	0.64	1.52	0.40	0.20	0.10
4-NO_2	150	0.44	0.65	1.50	0.40	0.20	0.10

[a] Concentration 5×10^{-5} mol dm^{-3}.

Table 2. Spectral data and p*K* values of 3-(*N*-nitro-*N*-arylhydrazono)pentane-2,4-diones in buffered solutions containing 35% (v/v) DMF.

R	λ_{max}/nm (acid form)	$\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}	λ_{max}/nm (base form)	$\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}	p*K*
H	296	8.7	398	11	8.2
2-OMe	298	12	398	7.8	8.3
4-OMe	296	30	400	6.9	8.5
2-Cl	296	32	398	12	8.3
3-Cl	300	17	405	6.3	8.3
2-CO_2H	296	18	400	9.2	8.2
4-Cl, 2-NO_2	298	22	388	9.2	8.4
4-NO_2	296	30	390	9.7	8.1

$$ArN(NHOH)N{=}CR_2 + 2e^- + 2H^+ \longrightarrow ArN(NH_2)N{=}CR_2 + H_2O \quad (3)$$

$$ArN(NH_2)N{=}CR_2 + 4e^- + 4H^+ \longrightarrow ArNHNH_2 + H_2NCHR_2 \quad (4)$$

Formation of phenylhydrazine strongly suggests that (**D**) rather than (**E**) is the reduced species.

1.0×10^{-3} mol dm^{-3} stock solutions of all these hydrazones were prepared in neat DMF.

Preliminary experiments were carried out with Britton–Robinson buffers. More detailed studies were carried out in simple buffers. The following buffers were used for the pH-ranges[42,43] indicated: (a) pH 2.3–3.7, $H_3PO_4 + NaH_2PO_4$; (b) pH 3.9–6.1, AcOH + AcONa; (c) pH 6.8–8.7, $NaH_2PO_4 + Na_2HPO_4$; (d) pH 9.4–12.1, $H_3BO_3 + Na_3BO_3$. pH Values of solutions were measured with a glass electrode in mixed solvents used in the experiments, using a glass electrode calibrated in the buffers having the mixed solvents used in the experiments.

Spectrophotometry.—Absorbance at 398 nm (*A*), measured on a UV VIS Specord Carl Zeiss spectrophotometer, in Britton–Robinson buffers containing 35% DMF and 1.0×10^{-4} mol dm^{-3} of the compound was used for determination of p*K* values using the expression[44] $pK = pH + \log [(A_{min} - A)/(A - A_{max})]$ (where A_{max} at pH < 6 and A_{min} at pH > 10). All the compounds (Table 1) have similar electronic spectra. They exhibit two absorption maxima, at 296 and 398 nm, the ratio of which remained independent of pH. With increasing pH the first maximum decreased up to pH 10.0. At higher pH values a pH-independent spectrum with a broad peak in the range 398–405 nm was observed (Table 2). IR spectra were scanned in KBr film on a Perkin-Elmer 577 spectrophotometer, NMR spectra on a Varian 270 MHz instrument, and mass spectra on a JEOL-JMS-DX 300 spectrophotometer.

Electrochemistry.—The polarograms were scanned on an Elico DC CL 25 pen-recording polarograph with capillary characteristics $m^{\frac{2}{3}}\ t^{\frac{1}{6}} = 3.62$ mg$^{\frac{2}{3}}$ s$^{\frac{1}{2}}$ at *h* 67 cm. A saturated calomel electrode was used as the reference electrode. The temperature coefficient was determined by Nejedlý's method.[45] In a typical polarographic experiment, *e.g.* when studying the influence of pH on the polarographic behaviour, a 5.0×10^{-5} mol dm^{-3} solution of these compounds was prepared by mixing the compound (0.5 cm^3; to 1×10^{-4} mol dm^{-3} in DMF), DMF (3.0 cm^3) (which was necessary to prevent precipitation), the appropriate buffer (5.5 cm^3), and tetraethylammonium bromide (NEt_4Br) (1.0 cm^3; to 1.0 mol dm^{-3}) as the supporting electrolyte. Polarograms were recorded after removal of oxygen, and currents were corrected for the residual current.

Cyclic voltammetric studies were carried out on a BAS CV-27 cyclic voltammograph in connection with a digital electronic Omnigraph *X–Y/t* recorder. A three-electrode system was used—glassy carbon (GC) as working, Ag/AgCl in 1.0 mol dm^{-3} KCl as reference and platinum wire as counter-electrode. The GC electrode was polished with fine-grade emery paper followed by polishing alumina (0.5 μm), washed, and activated by triangular voltage sweeps from +1.0 to −2.1 V at the rate of 5 and 200 mV min^{-1} for 15 min. The activity of the electrode was tested[46] using a solution of ferricyanide–ferrocyanide in 0.1 mol dm^{-3} KCl.

As the products of controlled-potential electrolysis (CPE) have been known to differ depending on the nature of the electrode employed,[47] electrolysis at a dropping mercury electrode (DME) was carried out in a microcell.[48] For coulometric determination[48] of the number of electrons

Table 3. Values of n determined by total coulometry, and composition of the products in preparative controlled-potential reduction of 3-(*N*-nitro-*N*-phenylhydrazono)pentane-2,4-dione at DME.

pH	*E* (Applied potential *vs.* SCE)		Analysis of products
2.5	−0.5	4.10	Hydroxylamine derivative (**I**)
	−1.2	8.20	Hydroxylamine derivative (**I**) Amino ketone (**III**)
	−1.8	10.25[a]	Phenylhydrazine (**II**) Amino ketone (**III**)
4.0	−1.2	8.00	Hydroxylamine derivative (**I**) Amino ketone (**III**)
	−1.8	10.30[a]	Phenylhydrazine (**II**) Amino ketone (**III**)
6.5	−1.8	10.10	Hydroxylamine derivative (**I**) Pentane-2,4-dione (**IV**) Ammonia
8.0	−1.8	10.12	Hydroxylamine derivative (**I**) Pentane-2,4-dione (**IV**) Ammonia
	−2.1	10.15	Hydroxylamine derivative (**I**) Pentane-2,4-dione (**IV**) Ammonia
10.2	−2.1	10.10	Hydroxylamine derivative (**I**) Pentane-2,4-dione (**IV**) Ammonia

[a] Possibly affected by simultaneous hydrogen evolution.

Table 4. Values of half-wave potentials and diffusion currents for 3-phenylhydrazonopentane-2,4-dione (I) and 3-(*N*-nitro-*N*-phenylhydrazono)pentane-2,4-dione (II) at different pH values (5×10^{-5} mol dm^{-3}; 35% DMF; 25 °C) under identical experimental conditions.

		(I)		(II)[a]	
No.	pH	$-E_{\frac{1}{2}}$/V	i_d/μA	$-E_{\frac{1}{2}}$/V	i_d/μA
1	2.5	0.59	0.20	0.60	0.20
2	3.8	0.61	0.25	0.62	0.25
3	4.5	0.64	0.25	0.64	0.20
4	6.5	0.67	0.20	0.65	0.20
5	8.5	0.68	0.20	0.67	0.20
6	10.5	0.69	0.20	0.67	0.20
7	12.0	0.69	0.25	0.68	0.20

[a] Values for the second wave corresponding to the reduction of the hydrazono group.

transferred in the electrode process an aliquot (2.0 cm^3) of solution of the compound containing buffer, solvent, and supporting electrolyte (in the same properties as was used in a typical polarographic experiment) was electrolysed at a potential which corresponds to individual limiting currents (Table 3). From the decrease of current with time during electrolysis, the number of electrons transferred was calculated. Progress of the electrolysis was monitored by recording of the polarographic reduction wave at different intervals of time.

Preparative electrolyses were carried out in solutions (2.0 cm^3) at a concentration of *ca.* 10^{-3} mol dm^{-3} at DME, keeping a blanket of nitrogen over the surface of the solution. The products of electrolysis were identified by comparison of their porperties with the expected products using an Aimil Nucon 5700 gas–liquid chromatograph. If products could not be isolated, their electrochemical oxidation was studied.

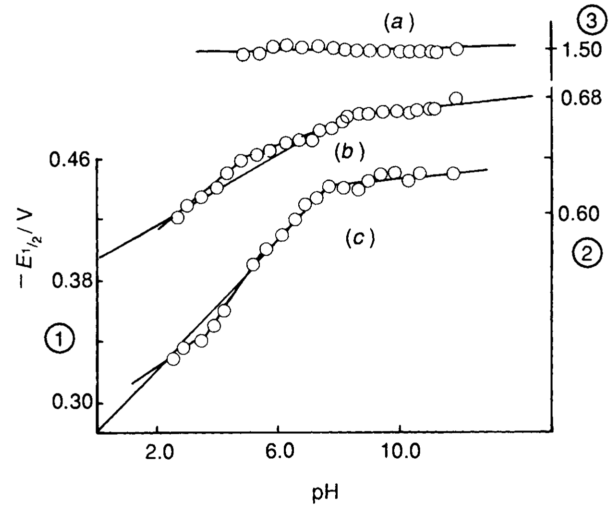


Figure 1. Plots of $-E_{\frac{1}{2}}$ *vs.* pH for 3-(*N*-nitro-*N*-phenylhydrazono)pentane-2,4-dione (0.5×10^{-4} mol dm^{-3}). (*a*) For nitro group, (*b*) for hydrazono group, (*c*) for C–N bond.

Results and Discussion

All the nitro hydrazono compounds (Table 1) exhibited two four-electron polarographic reduction waves in the pH range 2.0–4.0, and similarly two peaks in the initial scan in the cyclic voltammogram in this pH range. At higher pH values (pH > 4.0) one more wave involving two electrons in the DCP and one more peak in linear sweep voltammetry (LSV) was observed.

Polarographic Studies.—On the basis of the number of electrons involved in the electrode process and by comparing the wave-heights and $E_{\frac{1}{2}}$ values with the data of 3-(phenylhydrazono)pentane-2,4-dione which does not bear a nitro group on the hydrazono group under similar experimental conditions (Table 4), it was concluded that the second wave of the nitro compound is due to the reduction of the hydrazono group. A comparison of wave-heights and $E_{\frac{1}{2}}$-values with those for the first wave of the nitrobenzene or *p*-nitrobenzaldehyde under similar experimental conditions suggested that the first wave is due to a four-electron reduction of the nitro group[26] to a hydroxylamine. The third wave, involving two electrons and appearing at pH > 4.0 at more negative potentials, has been assigned to the reduction of an α-amino ketone formed at the 8-electron stage. Reduction of activated C–N bonds has been reported by other workers.[49,50]

Polarographic Behaviour of the Nitro and Hydrazono Groups.—The nitro group is reduced in a single four-electron wave at more positive potentials than is the hydrazono group. The limiting polarographic current due to the nitro group reduction was diffusion controlled.[51] Similarly, the diffusion-control nature of the reduction was confirmed for the second four-electron wave. For compounds (**7**) and (**8**) reductions of the two nitro groups overlap. Somewhat higher values of $i(d_1) + i(d_2)$ for compounds (**2**), (**5**), and (**6**) than expected for an 8-electron uptake, also observed for some other series,[52] may reflect reductions involving more than four electrons per step. The shift of half-wave potentials towards more negative potentials with increasing concentration of the depolarizer and logarithmic analysis confirmed the irreversible nature of both four-electron electrode processes.[51]

The half-wave potentials of these compounds were shifted towards more negative potentials with increase in pH (Figure 1). Several linear segments were observed at pH < *ca.* 8; at

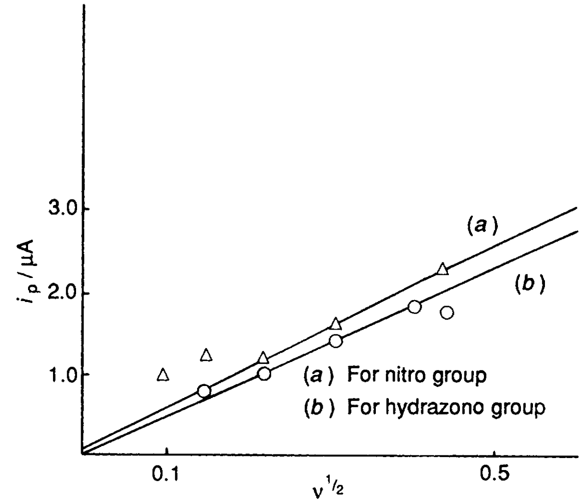


Figure 2. Plot of i_p *vs.* $v_{\frac{1}{2}}$ for 3-(*N*-nitro-*N*-phenylhydrazono)pentane-2,4-dione a pH 2.5 (0.5 × 10^{-4} mol dm^{-3}).

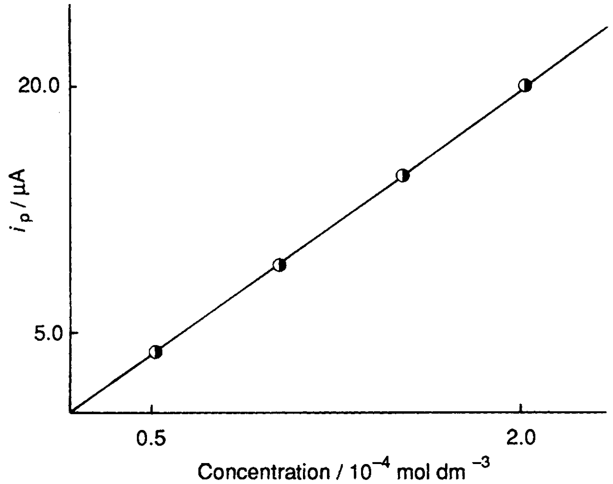


Figure 3. Plot of i_p *vs.* concentration for the reduction of the nitro group of 3-(*N*-nitro-*N*-phenylhydrazono)pentane-2,4-dione at pH 5.6.

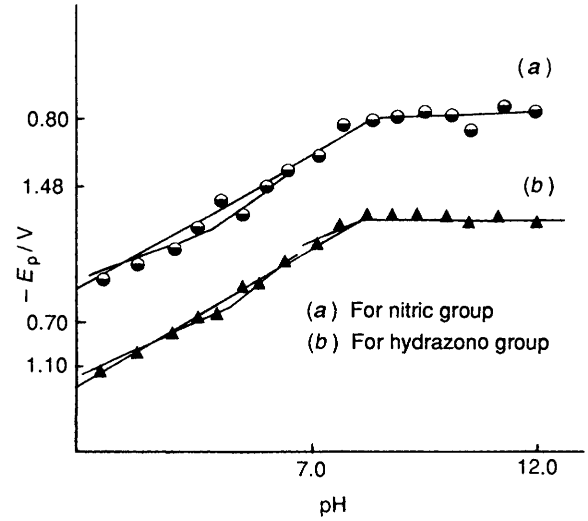


Figure 4. Plots of E_p *vs.* pH for 3-(*N*-nitro-*N*-phenylhydrazono)pentane-2,4-dione (0.5 × 10^{-4} mol dm^{-3}).

higher pH the values of $E_{\frac{1}{2}}$ became practically constant. Coulometric measurements confirmed that in acidic solutions (pH < 4.0) two four-electron steps occur, corresponding to the reduction of the nitro group to a hydroxylamino group and to the reduction of the hydrazono group, respectively. No wave corresponding to a two-electron reduction of the hydroxylamino to an amino group has been observed in the pH-range studied and no phenylhydrazine has been detected among reduction products formed at −0.5 V and −1.2 V. Coulometry at −1.8 V in this pH-range indicated transfer of 10 electrons and at this potential phenylhydrazine was identified among the reduction products, probably formed in a potential region where reduction of hydrogen also occurs in a competitive process. At pH > 4.0 phenylhydrazine could not be detected among the reductions products at −1.8 V or even at −2.0 V. Under such conditions coulometry suggests that the overall process involves 10 electrons. In this pH-range the additional two-electron transfer (following that of the first 8 electrons) has been attributed to the reduction of the α-amino ketone formed in the 8-electron stage.

Polarographic Reduction of the α-Amino Ketone formed at 8-*Electron Stage.*—The third wave observed at pH > 4.0 corresponds to a two-electron reduction of the C–N bond facilitated by the presence of two activating CO groups.[49,50] The reduction of the C–N bond was confirmed by CPE; gas chromatographic analysis enabled identification of pentane-2,4-dione as one of the electrolysis products. In the solution after electrolysis ammonia was detected by Nessler reagent.[53]

Both the height and half-wave potential of this wave were pH independent and the wave is irreversible. The pH independence of $E_{\frac{1}{2}}$ indicates that the pK_a value of the ammonium form of the amino diketone is > *ca.* 11. By analogy with other substances[49] bearing a C–N bond, the formation of NH_3 results probably from the reduction of the protonated form.

Linear Sweep and Cyclic Voltammetry.—Cyclic voltammograms of nitro hydrazono compounds recorded at different scan rates (20 mV s^{-1} to 200 mV s^{-1}) and concentrations using mercury film and glassy carbon electrodes exhibit two well defined cathodic peaks in the pH range 2.0–4.0. This behaviour is in agreement with that observed from polarographic measurements. The linear plots of peak current (i_p) *vs* the square root of sweep rate ($v^{\frac{1}{2}}$) (Figure 2) and i_p *vs* concentration (Figure 3) show little deviation from the origin, indicating that electrode reaction is mainly diffusion-controlled[54] for both the waves. Peak potentials show shifts towards negative potential with pH, with several linear segments up to pH 7.5 for the first peak and up to pH 8.0 for the second peak, and are practically pH independent at higher pH values (Figure 4). On reversing the first scan no anodic peak could be observed, indicating that the processes corresponding to both peaks are irreversible. However, in second and subsequent scans a reversible redox couple (−0.30 to −0.36 V) corresponding to the oxidation of arylhydroxylamine and reduction of the resulting nitroso compound was observed (Figure 5), as for other nitro compounds.[55]

At pH > 4.0 the nitro hydrazono compound gives three peaks. The first two peaks are irreversible, diffusion controlled, and shifted towards negative potential with pH whereas the third peak was pH independent. In the second scan a hydroxylamino–nitroso redox couple was also observed (Figure 5) but not other peak, even at higher sweep rates (250 mV s^{-1}), could be observed. Total currents $i(p_1)$ and $i(p_2)$ remained constant over the entire pH-range studied.

The first main peak was attributed to the reduction of the nitro group to a hydroxylamino group. The second peak has

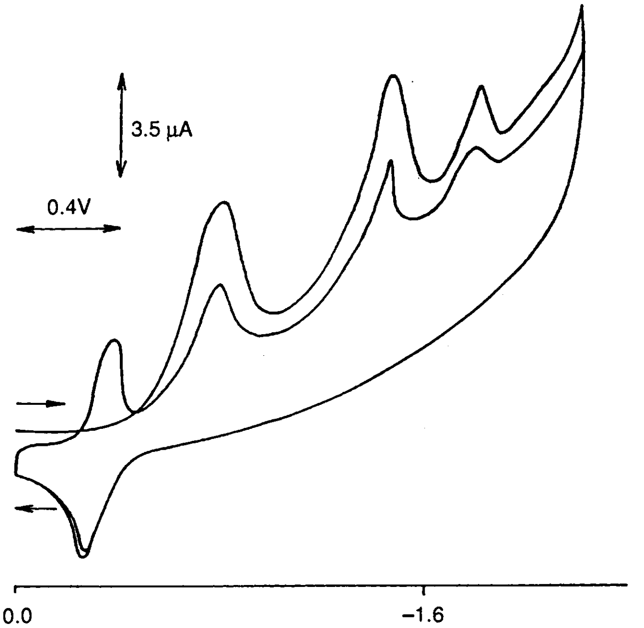


Figure 5. Cyclic voltammograms of 0.5×10^{-4} mol dm^{-3} 3-(*N*-nitro-*N*-phenylhydrazono)pentane-2,4-dione at pH 8.5; scan rate 200 mV s^{-1}.

been assigned to the reduction of the hydrazono group, the third at pH > 4.0 to the irreversible reduction of the N–C bond.

Coulometry and Product Analysis.—The values of *n* and products determined at different pH values and at different potentials are summarized in Table 3. The four-electron electrolysis at −0.5 V, pH 2.5 and 4.0, resulted in a single product, as shown by TLC. Based on electrochemical oxidation its structure is assumed to be the *N*-hydroxylamino derivative **I**. The eight-electron electrolysis at −1.2 V at these two pH values yielded two compounds, with R_f 0.26 and 0.69. One of these compounds is the hydroxylamino derivative (**I**), as confirmed by its electro-oxidation. The other compound was identified as $H_2NCH(COMe)_2$, as confirmed by IR (NH_2 3 410 and 1 610 cm^{-1}; CH 2 670 cm^{-1}; C=O 1 615 cm^{-1}) and ^1H NMR [δ 1.5 (1 H, s, CH), 2.5 (6 H, s, 2 Me), and 3.7 (2 H, s, NH_2)] spectra in $CDCl_3$. The proposed structure was further supported by mass spectra (*m/z* 115) and elemental analysis (Found: C, 52.3; H, 8.0; N, 12.3. Calc. for $C_5H_9NO_2$: C, 52.17; H, 7.82; N, 12.17%).

Electrolysis at more negative potentials (−1.8 V), at pH 2.5 and 4.0 yielded, in addition to the amino ketone, another product, identified as phenylhydrazine ($C_6H_5NHNH_2$) (**II**) by comparison with an authentic reference specimen, and the number of electrons involved in the overall process was found to be 10.0.

CPE with DME in a small volume (2.0 cm^3) of the 1×10^{-3} mol dm^{-3} solution of nitro hydrazones in buffers of pH 2.0–4.0 at −1.80 V showed a linear plot of log *i* against *t*. This indicated that that products of electrolysis were not involved in consecutive reactions, *e.g.* of one of the product hydroxylamines (**I**) with the carbonyl groups present or with the azomethine bond. Absence of an additional peak in the UV–visible spectra of the solution during electrolysis indicated absence of an absorbing intermediate with sufficient half-life.

CPE at pH 6.5 at −1.8 V and at pH 8.0 and 10.2 at −2.1 V and subsequent product analysis confirmed the presence of the hydroxylamino derivative (**I**), pentane-2,4-dione (**IV**), and ammonia. The presence of pentane-2,4-dione was confirmed by comparison with an authentic sample by GLC (t_R 2.75 min, on a XE-60 column); ammonia was detected by Nessler's reagent. The number of electrons involved in the overall process was found to be 10 ± 0.20. For confirmation of this behaviour, 3-aminopentane-2,4-dione was taken separately and its 1.0×10^{-3} mol dm^{-3} solution in an identical polarographic solution was electrolysed at −2.1 V (DME). The presence of ammonia and pentane-2,4-dione (**IV**) in the electrolysed solution confirmed the cleavage of the C–N bond.

Redox Mechanism.—On the basis of DCP, LSV, and CPE the following mechanism may be proposed for the reduction of these nitro compounds. At pH < 4.0 the reduction of the nitro group follows equations (5) and (6), while at pH > 4.0 equation (7) holds.

$$\mathrm{ArNR{\cdot}NO_2 + 4e^- + 4H^+ \longrightarrow \underset{(I)}{ArNR{-}NHOH} + H_2O} \quad (5)$$

$$\mathrm{ArNR{-}NHOH + 2e^- + 2H^+ \longrightarrow \underset{(II)}{ArNRNH_2} + H_2O} \quad (6)$$

$$\mathrm{ArNR{-}NO_2 + 4e^- + 4H^+ \longrightarrow \underset{(I)}{ArNR{-}NHOH} + H_2O} \quad (7)$$

Where R = N=C(COMe)$_2$

In acidic media (pH < 7.6) di- and mono-protonated forms are reduced as is evident from $E_{\frac{1}{2}} = f(\mathrm{pH})$ plots (Figure 1). However, in alkaline media (pH > 7.6) the first step is the formation of radical anion (by the uptake of one electron) which undergoes further electron transfer and then protonation, resulting in the formation of the hydroxylamine. Similar observations have been made in other alkaline solutions.[56,57]

For reduction of the C=N bond (assuming ArNRNHOH as the product) equations (8) and (9) can be proposed.

$$\mathrm{ArN(NHOH){-}N{=}C(COMe)_2 + H^+ \rightleftharpoons ArN(NHOH){-}\overset{+}{N}{=}C(COMe)_2} \quad (8)$$

$$\mathrm{ArN(NHOH){-}\overset{+}{N}H{=}C(COMe)_2 + 4e^- + 3H^+ \longrightarrow ArNHNHOH + \underset{(III)}{H_2NCH(COMe)_2}} \quad (9)$$

A similar mechanism has also been reported for the reduction of other hydrazones.[1,2] At pH > 4.0, $H_2NCH(COMe)_2$ (**III**) undergoes further reduction as shown by equation (10).

$$\mathrm{H_2NCH(COMe)_2 + 2e^- + 2H^+ \longrightarrow H_3N + \underset{(IV)}{CH_2(COMe)_2}} \quad (10)$$

Product analysis at pH > 4 at −2.1 V confirmed the presence of hydroxylamine derivative (**I**), pentane-2,4-dione (**IV**), and ammonia, and the absence of phenylhydrazine (**II**) among the products of electroreduction indicated the involvement of 10 electrons in the overall electrode process. The presence of the hydroxylamine derivative and the absence of the phenylhydrazine in the products of electrolysis at pH > 4, indicated that the hydroxylamino group did not undergo further reduction but that the 3-aminopentane-2,4-dione (**III**) was further reduced in the third wave to give pentane-2,4-dione (**IV**) and ammonia. Such reductions of activated C–N bonds have previously been reported.[49,50]

On the basis of these mechanistic studies and the number of electrons involved in the reduction, a structure for these nitro compounds having an azo group (**E**) can be excluded. The second four-electron transfer and the nature of the reduction products point towards a hydrazono structure (**D**).

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