POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF 1-(2′-NITROPHENYL)-3,3-DIMETHYLTRIAZENE*

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The polarographic behaviour of 1-(2′-nitrophenyl)-3,3-dimethyltriazene in a mixed aqueous-methanolic solvent was investigated by tast polarography, differential pulse polarography, and fast scan differential pulse voltammetry at a hanging mercury drop electrode. A mechanism is suggested for the reduction of the compound investigated. The optimum conditions were found for the determination of this analyte by tast polarography over the concentration region of 100 to 2 μmol l^{-1} and by differential pulse polarography or fast scan differential pulse voltammetry at a hanging mercury drop electrode over the region of 100 to 0.2 μmol l^{-1}. Additional sensitivity increase in the last-mentioned technique was achieved by adsorptive accumulation of analyte on the hanging mercury drop surface, owing to which the concentration region was depressed to 0.1 – 0.02 μmol l^{-1}.

1-Phenyl-3,3-dimethyltriazene derivatives are genotoxic substances[1] which, however, also exhibit carcinostatic effects[2,3]. Analytical methods capable of quantitating trace amounts of such substances are therefore increasingly required. With regard to the easy polarographic reducibility of the triazene group[4], we have been concerned with the applicability of differential pulse polarography (DPP) at the conventional dropping mercury electrode (DME), fast scan differential pulse voltammetry (FSDPV) at a hanging mercury drop electrode (HMDE), and adsorptive stripping voltammetry (AdSV) to the determination of pharmaceutically relevant carboxylamido derivatives of 1-phenyl-3,3-dimethyltriazene[5 – 7]. Polarographically interesting is the behaviour of 1-phenyl-3,3-dimethyltriazene derivatives carrying additional polarographically active substituents that can contribute to the sensitivity of the polarographic or voltammetric quantitation, as is the case with 1-[4′-phenylazo)phenyl]-3,3-dimethyltriazene[8,9].

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The present paper is concerned with the polarographic and voltammetric determination of 1-(2′-nitrophenyl)-3,3-dimethyltriazene (*I*) [CAS Name: 1-Triazene, 3,3-dimethyl-1-(2′-nitrophenyl); CAS Registry Number: 20241-01-4]. The triazene group and the nitro group in the ortho position of the aromatic ring can interact in this compound and thus facilitate the electron interaction of the two polarographically active groups. Such interaction can affect not only the polarographic reduction of the triazene group (whose mechanism has been discussed, e.g., in the monograph[4]), but also that of the nitro group. The mechanism of polarographic reduction of nitro groups has been dealt with in detail, e.g., in the monographs[10 – 14] and in the review[15].

In view of the sparing solubility of the solute in water, a mixed aqueous-methanolic solvent was used, as has proved convenient for other 1-phenyl-3,3-dimethyltriazene derivatives[5 – 9,16 – 18].

EXPERIMENTAL

Reagents

1-(2′-Nitrophenyl)-3,3-dimethyltriazene, pure grade, was obtained from the Research Institute of Organic Syntheses in Pardubice-Rybitví. A stock solution (c = 1 mmol l^{-1}) was prepared by dissolving 0.0194 g of the substance in solvent of reagent grade purity and diluting to 100 ml. More dilute solutions were obtained by diluting this stock solution with methanol. The purity of the chemical used was checked by paper and thin layer chromatography and by UV-VIS spectral measurement[19]. All solutions were kept in dark. Solutions in methanol at c = 1 and 0.1 mmol l^{-1} exhibited absorbance which was stable, within experimental error, for at least one week. The absorbance of the solutions with c = 1 and 0.1 mmol l^{-1} decreased 2.0% in 20 days and 3.2% and 3.8%, respectively, in 40 days. More dilute solutions (0.01 mmol l^{-1} and lower) were newly prepared every day. The other chemicals used were of reagent grade purity (Lachema, Brno). Water was redistilled twice in a quartz still. Britton–Robinson buffers, prepared conventionally, were stored in glass vessels solely because they extract from polyethylene substances that affect adversely the adsorptive stripping voltammetric determination.

Apparatus

A PA 4 polarographic analyzer interfaced to an XY 4105 recorder (Laboratorní přístroje, Praha) was used in the three-electrode connection involving a saturated calomel reference electrode and a platinum sheet auxiliary electrode. All potentials reported herein refer to the saturated calomel electrode. The potential sweep rate for the DC, tast and DP polarography at a DME was 5 mV s^{-1}. The controlled drop time was 1 s, the mercury reservoir height was 49 cm, and the modulation amplitude in the DPP mode was −100 mV, unless stated otherwise. The dropping electrode flow rate was 0.97 mg s^{-1} and the drop time was 6.46 s (measured in 0.1 M KCl at 0 V applied voltage).

FSDPV and cyclic voltammetric measurements were carried out using an SMDE 1 working mercury electrode (Laboratorní přístroje, Praha) with a capillary 0.140 mm in diameter, connected as an HMDE. Unless stated otherwise, the potential sweep rate was 20 mV s^{-1}, the maximum drop size was determined by the valve opening period of 160 ms, the modulation amplitude in the FSDPV mode was −100 mV.

Oxygen was removed from the solutions by nitrogen purging for 10 min; nitrogen for this application was purified by passing it through a solution of chromium(II) ions in dilute hydrochloric acid over zinc amalgam and subsequently through a methanol–water mixture of the same composition as used as the solvent.

The solution pH was measured with a PHM 62 instrument (Radiometer, Copenhagen) using a glass electrode and a saturated calomel electrode. The true pH of the Britton–Robinson buffer mixture with methanol was determined as described previously[6].

Spectrophotometric measurements were conducted on a PU 8800 instrument (Pye Unicam, U.K.) using 1 cm quartz cells.

Coulometric measurements were performed on an OH 404 coulometric analyzer (Radelkis, Budapest) in a 200 ml vessel. A mercury pool at the vessel bottom served as the cathode, a platinum sheet electrode served as the anode. The cathode and anode compartments were separated with a frit. The saturated calomel reference electrode used was an OH 933 (Radelkis, Budapest). The solution was stirred with a magnetic stirrer during the electrolysis, and the measurements were conducted under nitrogen.

All measurements proceeded at room temperature.

Procedures

A volume of the 1-(2′-nitrophenyl)-3,3-dimethyltriazene solution in methanol at the requisite concentration was pipetted into a 10 ml volumetric flask, methanol was added so that the total volume was 5 ml, and the whole was diluted to the mark with the Britton–Robinson buffer of the desired pH. (This order had to be adhered to because if, conversely, the analyte solution is added to the aqueous buffer, the analyte can separate from the solution.)

The calibration curves were measured in triplicate and evaluated by linear regression using the least squares method. The limit of determination was calculated as the tenfold standard deviation from 7 analyte determinations at the concentration corresponding to the lowest point of the calibration dependence.

The procedure for the determination of the number of exchanged electrons was as used previously[8].

RESULTS AND DISCUSSION

Mechanism of Polarographic Reduction of 1-(2′-Nitrophenyl)-3,3-dimethyltriazene

Tast polarography of 1-(2′-nitrophenyl)-3,3-dimethyltriazene in a Britton–Robinson buffer–methanol mixture (1 : 1) gives one to three waves in dependence on pH (Table I). The waves shift to more negative potentials with increasing pH, which indicates that protonation precedes.

The 1st wave occurs across the entire pH region. Its half-wave potential (in mV) obeys the relation $E^1_{1/2} = -68 - 59$ pH over the region of pH 2 – 8 (correlation coefficient $r = 0.9897$). The $E^1_{1/2}$ shift is considerably more marked at pH 8 – 10, whereas at pH > 10 the half-wave potential remains constant. The semilogarithmic analysis slope at pH 1 and pH 7 is about −60 mV, which indicates that an irreversible process accompanied by the exchange of the same number of protons and electrons is involved. The wave height is about one-half higher in acid solutions (pH < 2) than in basic solutions (Fig. 1). The reversibility of the wave decreases appreciably at pH 8 – 10 and a hint of its splitting into two waves of equal height is observed, whereas a single wave occurs again at pH > 10; the slope of its semilogarithmic analysis is about 55 mV, indicating again the occurrence of an irreversible process accompanied by the exchange of identical numbers of protons and electrons. At each pH, the wave height remains constant within 1 h from the preparation of the polarographed solution.

Within the region of pH 3 – 6, the wave splits into two, with the height ratio about 2 : 1, the total height of the two waves being roughly constant. (The lower height values for the 2nd wave given in Table I are rather due to the evaluation procedure, which is complicated by the fact that the straight lines drawn through the limiting currents of waves 1 and 2 fail to be parallel.) The 2nd wave vanishes at pH > 6. The height of the 2nd wave also remains constant with time within 1 h from the preparation of the polarographed solution.

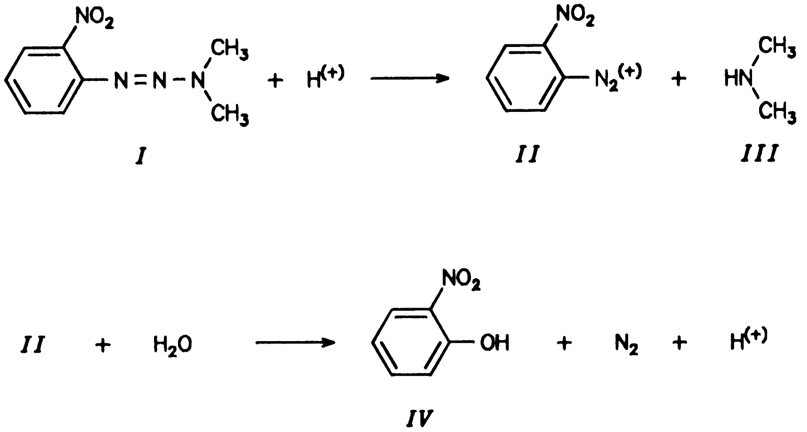
TABLE I

Effect of pH on the polarographic behaviour of 1-(2′-nitrophenyl)-3,3-dimethyltriazene (c = 100 μmol l^{-1}) in Britton–Robinson buffer–methanol mixtures (1 : 1)

pH[a]	$E^1_{1/2}$, mV	I^1_{lim}, μA	α_1[b]	$E^2_{1/2}$, mV	I^2_{lim}, μA	α_2[b]	$E^3_{1/2}$, mV	I^3_{lim}, μA	α_3[b]
1.0[c]	-95	0.83	61	[e]	[e]	[e]	-725	0.19	34
2.0[d]	-180	0.83	47	[e]	[e]	[e]	-755	0.44	36
2.6	-260	0.41	[f]	-385	0.05	[f]	-825	0.46	36
4.0	-320	0.45	45	-560	0.12	[f]	-910	0.46	46
4.7	-355	0.45	44	-625	0.10	[f]	-965	0.44	49
5.8	-400	0.51	50	-700	0.05	[f]	-1 060	0.48	63
6.9	-470	0.49	62	–	–	–	-1 200	0.71	81
8.0	-530	0.50	93	–	–	–	-1 220	0.39	62
8.7	-675[g]	0.51[g]	[g]	–	–	–	-1 230	0.18	57
9.7	-815[g]	0.55[g]	[g]	–	–	–	–	–	–
10.1	-875	0.59	80	–	–	–	–	–	–
11.1	-905	0.58	56	–	–	–	–	–	–
12.1	-900	0.59	55	–	–	–	–	–	–
13.7	-890	0.60	53	–	–	–	–	–	–

[a] Resulting pH of buffer or perchloric acid mixture with methanol; [b] semilogarithmic analysis slope; [c] adjusted with 1 M $HClO_4$; [d] adjusted with 0.1 M $HClO_4$; [e] 1st and 2nd wave merge; [f] semilogarithmic analysis is impossible because the two waves are poorly resolved and the 2nd wave has a very protracted shape; [g] semilogarithmic analysis is impossible because of wave splitting, the $E_{1/2}$ value is approximate only, the limiting current corresponds to the total height of the split wave.

The 3rd wave is present at pH 2 – 9 and its height is constant within the region of pH 3 – 7. (The observed higher value at pH 6.9, given in Table I, is again due to the evaluation procedure for this wave of a somewhat atypical shape – Fig. 1, curve *6* – determined by the limiting current decrease with increasing potential.) The limiting current of the 3rd wave decreases with increasing potential at pH > 7; the wave gradually adopts a shape of a broad peak whose height decreases with increasing pH and which vanishes altogether at pH > 9. The height and shape of this wave are virtually time-invariable at pH 3 – 9, whereas the height decreases 10% and 85% in 1 h at pH 2.0 and pH 1.0, respectively. The time changes in the tast and DP polarograms of 1-(2′-nitrophenyl)-3,3-dimethyltriazene at pH 1.0 are documented by Fig. 2. As the height of the 3rd wave decreases, so does the 1st wave, and a new wave with a half-wave potential which is about 150 mV more negative appears. This wave is presumably due to *o*-nitrophenol (*IV*) formed by acid-catalyzed hydrolysis according to Eqs (*A*).



(*A*)

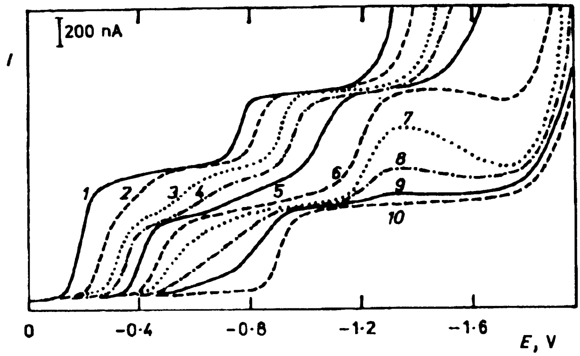


FIG. 1
Tast polarograms of 1-(2′-nitrophenyl)-3,3-dimethyltriazene (c = 100 μmol l^{-1}) in Britton–Robinson buffer–methanol mixtures (1 : 1); pH: *1* 2.0, *2* 2.6, *3* 4.0, *4* 4.7, *5* 5.8, *6* 6.9, *7* 8.0, *8* 8.7, *9* 9.7, *10* 11.1

Owing to the +M effect of the OH group, which poses a hindrance to the reduction of the nitro group, the hydrolysis product exhibits a half-wave potential which is more negative than that of the starting triazene nitro derivative where, on the contrary, the reduction of the nitro group is facilitated by the −M effect of the triazene group. This assumption is borne out by the tast and DP polarograms of authentic *o*-nitrophenol (curves *3* in Fig. 2) as well as by the fact that in a certain time, the solution of 1-(2′-nitrophenyl)-3,3-dimethyltriazene exhibits an anodic wave (curve *2* in Fig. 2*a*) which can be attributed to the reaction of mercury with the forming dimethylamine (*III*). The 3rd wave recorded immediately after purging the solution to be polarographed (10 min after preparation) is substantially lower at pH 1.0 than at pH 3 – 6. This indicates a fast course of the acid catalyzed hydrolysis, owing to which the major fraction of the substance decomposes as early as the nitrogen purging. The half-wave potential of the 3rd wave (in mV) obeys the relation $E_{1/2}^3 = -610 - 76.7$ pH across the region of pH 2 – 6 ($r = 0.9963$). The different semilogarithmic analysis slope and the $E_{1/2}^3$ vs pH plot slope indicate that the process involved is no simple irreversible process accompanied by the exchange of the same number of electrons and protons; rather, it is a more complex process which probably involves adsorption of the substance on the working electrode surface. The half-wave potential is virtually pH-independent at pH > 7, at which the wave height decrease with increasing pH begins to appear.

The dependence of the height of the 1st wave, measured by DC polarography, on the square root of the mercury reservoir height is linear in Britton–Robinson buffer–methanol 1 : 1 mixtures at pH 3 – 13 and passes through the origin, which gives evidence that a diffusion-controlled process is involved. This is also true of the 3rd wave at pH 3 – 6.

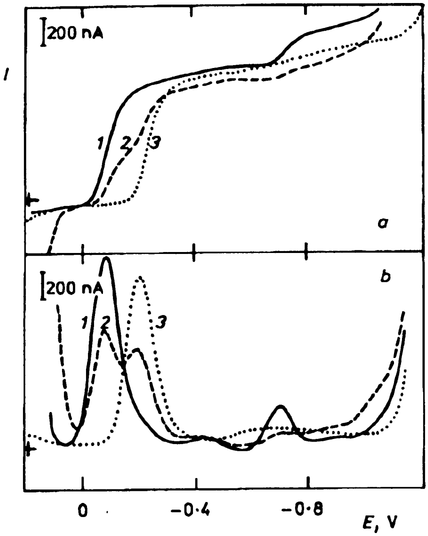


Fig. 2

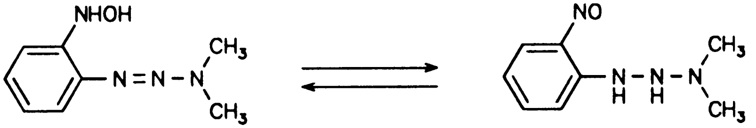
Tast (*a*) and DP (*b*) polarograms of 1-(2′-nitrophenyl)-3,3-dimethyltriazene (c = 100 μmol l^{-1}) in 1 M $HClO_4$–methanol mixture (1 : 1) at pH 1.0, measured 10 min (*1*) and 60 min (*2*) after preparation of the polarographed solution, and polarograms of *o*-nitrophenol (c = 100 μmol l^{-1}) in the same medium (*3*). The current zero position is indicated with a cross

This dependence ceases to pass through the origin at pH > 7, and the height of the 3rd wave is virtually independent of the mercury reservoir height at pH 8.7, indicating kinetic control of the process. Based on analogy with the polarographic behaviour of the 1-phenyl-3,3-dimethyltriazene derivatives studied previously[5 - 9,17,20] as well as of aromatic nitro compounds[10 - 15,21,22] we suggest that the 3rd wave is due to the reduction of the triazene group whereas the 1st wave is due to the reduction of the nitro group and the 2nd wave is associated with the reduction of the transient hydroxylamine group.

Potentiostatic Coulometry

Coulometry at a mercury pool in Britton–Robinson buffer–methanol mixtures 1 : 1 at pH 5.0 gave values of n = 4.2, 5.2 and 9.0 at constant potentials of −0.5, −0.8 and −1.1 V, respectively, corresponding to the limiting currents of the 1st, 2nd and 3rd wave, respectively. At pH 11.1, the obtained n value at −1.1 V, corresponding to the limiting current of the 1st wave, was 4.6, whereas at pH 2.0 this value was 6.2 at a constant potential of −0.4 V corresponding to the limiting current of the 1st wave. At −1.0 V, which corresponds to the limiting current of the 2nd wave at this pH, the n value was poorly reproducible, lying within the range of 8 to 9; this is apparently associated with the above-mentioned acid-catalyzed decomposition of the triazene group.

The fast polarographic examination of the coulometric reduction of 1-(2′-nitrophenyl)-3,3-dimethyltriazene at pH 5.0 (Fig. 3) showed that, irrespective of the constant potential applied, the 3rd wave, which is attributed to the triazene group, vanishes as well. This can be explained in terms of the rapid decomposition of the triazene group after the stabilizing effect of the nitro group, which is eliminated by the reduction, ceases to occur. The mesomeric interaction of the triazene group with the hydroxylamine group formed by the reduction of the nitro group (Eq. (*B*)) can also play a role.

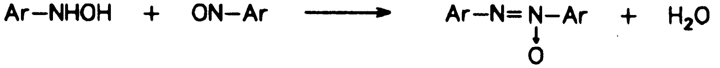


V VI (*B*)

Apparently, the nitroso compound so emerging is then reduced at more positive potentials than 1-(2′-nitrophenyl)-3,3-dimethyltriazene is, so that the corresponding wave merges with that of the nitro group and increases somewhat the observed number of exchanged electrons.

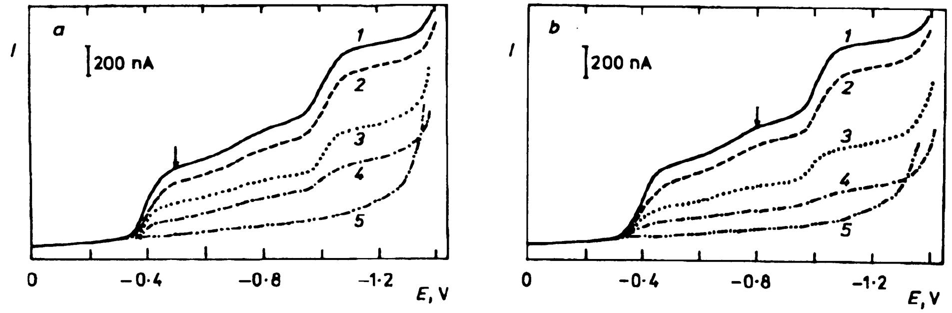
The fast polarographic monitoring of the coulometric reduction of the substance at pH 11.1 and at a constant potential of −1.1 V (Fig. 4) reveals the formation of products which give anodic waves with half-wave potentials about −0.45 and −0.27 V. Allowed to stand in the presence of air oxygen, the system gives rise to a cathodic wave which makes a nearly reversible pair with the anodic wave at –0.45 V (curve *4* in Fig. 4).

The nature of the anodic waves is discussed in the paragraph on cyclic voltammetry. During a longer coulometric experiment in basic solutions, the formation of azoxybenzene[23] (Eq. (*C*)) or of azobenzene, hydrazobenzene or benzidine derivatives[24] can also play a role.



$$\text{Ar–NHOH} + \text{ON–Ar} \longrightarrow \text{Ar–N}{=}\underset{\substack{\downarrow\\ \text{O}}}{\text{N}}\text{–Ar} + H_2O \qquad (C)$$

Based on analogy with unsubstituted phenylhydroxylamine[25] and with regard to the –M effect of the triazene group facilitating the reduction of the –NHOH group, the above anodic wave at –0.45 V appearing at pH 11.1 can be attributed to the reversible anodic oxidation of the hydroxylamine group to a nitroso group, whereas the anodic wave at –0.27 V seems to belong to the anodic oxidation of the possible products of condensation or dimerization reactions of the transient intermediates.



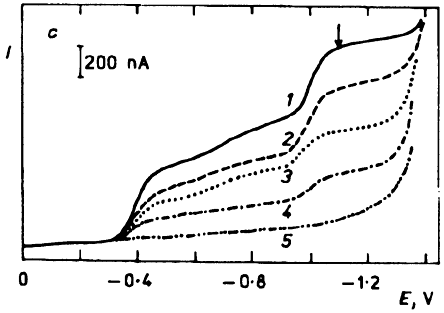


FIG. 3

Tast polarographic monitoring of the coulometric reduction of 1-(2′-nitrophenyl)-3,3-dimethyltriazene (c = 100 μmol l^{-1}) in Britton–Robinson buffer–methanol mixture (1 : 1) at pH 5.0. Constant potential of –0.50 V (*a*), –0.80 V (*b*) and –1.10 V (*c*). Curves correspond to the passage of charge required to reduce 0% (*1*), 25% (*2*), 50% (*3*), 75% (*4*) and 100% (*5*) of the substance (calculated with respect to the n value established at the potential applied). Arrow indicates potential at which the coulometric reduction was conducted

Spectrophotometric examination of the coulometric reduction at pH 5.0 (Fig. 5*a*) shows that the absorbance of the peak at 276 nm, which we attribute to the conjugated nitro and triazene group system, decreases at all of the three constant potentials applied. A maximum at 305 nm appears after reduction at −0.5 V (Fig. 5*a*, curve *2*), which is apparently associated with the unreduced triazene group[19]. This is borne out by the fact that this maximum also nearly vanishes during reduction at −0.8 or −1.1 V (curves *3* and *4*). Three new absorption peaks appear after exhausting electrolysis at −1.1 V in solution at pH 11.1 (Fig. 5*b*). We attribute the band at 320 nm to the triazene group, the

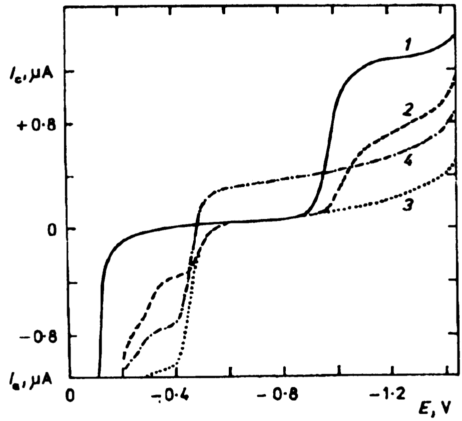


Fig. 4

Fast polarographic monitoring of the coulometric reduction of 1-(2′-nitrophenyl)-3,3-dimethyltriazene (c = 100 μmol l^{-1}) in Britton–Robinson buffer–methanol mixture (1 : 1) at pH 11.1. Constant potential of −1.10 V. Curves correspond to the passage of charge corresponding to 0 (*1*), 2.3 (*2*), and 4.6 (*3*). Curve *4* was obtained with solution which was reduced completely and allowed to stand for 5 min in the presence of air oxygen

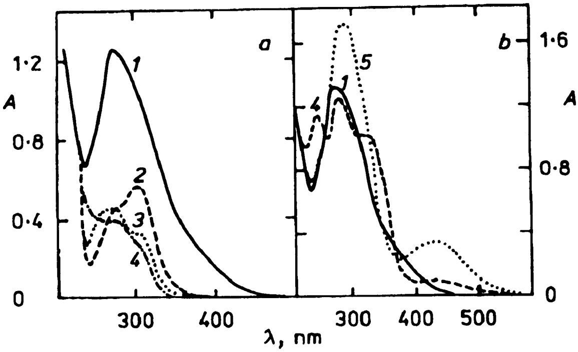


Fig. 5

Spectrum of solution of 1-(2′-nitrophenyl)-3,3-dimethyltriazene (c = 100 μmol l^{-1}) in Britton–Robinson buffer–methanol mixtures (1 : 1) at pH 5.0 (*a*) and pH 11.1 (*b*) before commencing coulometric reduction (*1*), after exhausting electrolysis at potentials of −0.5 V (*2*), −0.8 V (*3*) and −1.1 V (*4*), and after oxidation of the coulometric reduction products by contact with air oxygen for 1 min (*5*) reduction of the nitro group causing a shift to higher wavelengths. The band at 259 nm is assigned to the –NHOH group, emerging from the four-electron reduction of the nitro group. This concept is supported by the fact that the latter band vanishes during the oxidation of the coulometric reduction products by air oxygen and a new band appears at 428 nm, which is apparently due to the presence of the nitro group formed by oxidation of the hydroxylamine group by air oxygen. The conjugation of the nitroso group with the triazene group then is apparently responsible for the bathochromic and hyperchromic shift of the band (Fig. 5*b*, curve *5*).

Cyclic Voltammetry

Cyclic voltammograms of 1-(2′-nitrophenyl)-3,3-dimethyltriazene at pH 2.8 (Fig. 6*a*) demonstrate that none of the three cathodic peaks corresponds to a reversible process. Peak with E_p = –0.38 V is attributed to the reduction of the nitro group whereas peak with E_p = –0.95 V is attributed to the reduction of the triazene group. The middle peak (E_p = –0.52 V) apparently corresponds to the 2nd wave in the tast polarograms, whose possible origin has been discussed above. The observed anomalies during the reverse

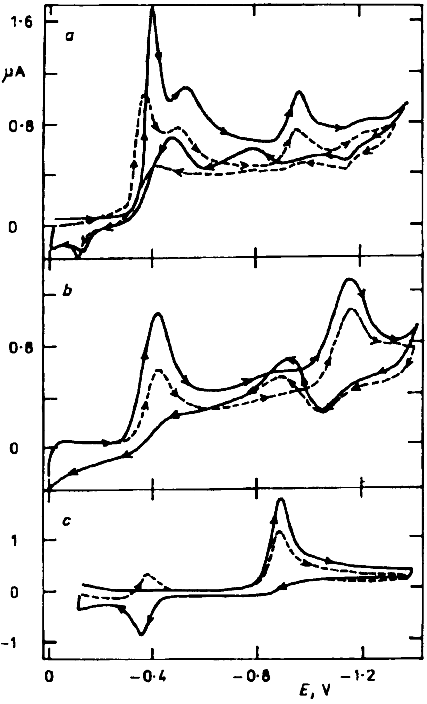


Fig. 6

Cyclic voltammograms of 1-(2′-nitrophenyl)-3,3-dimethyltriazene (c = 100 μmol l^{-1}) in Britton–Robinson buffer–methanol mixtures (1 : 1) at pH 2.8 (*a*), 4.9 (*b*) and 11.0 (*c*). Polarization rate 50 mV s^{-1} (*a*, *b*) or 100 mV s^{-1} (*c*). Full and broken lines refer to the 1st and 2nd cycles, respectively scan are presumably due to the adsorption of the starting substance or of the electrode reaction products on the HMDE surface. Only two peaks appear at pH 4.9 (Fig. 6*b*); one, with $E_p = -0.42$ V, is assigned to the reduction of the nitro group, the other, with $E_p = -1.15$ V, to the reduction of the triazene group. The latter peak exhibits a hint of reversibility. The anomalies within the region of −0.8 to −1.0 V are again ascribed to adsorption of the starting substance or the electrode reaction product at the HMDE surface, which can cause "in situ" modification of the electrode and bring about shift of the 2nd peak towards more positive potentials due to the increased rate of the preceding surface protonation. At pH 11.0, the cyclic voltammogram exhibits a single cathodic peak with $E_p = -0.89$ V during the first cycle (Fig. 6*c*), which we attribute to the irreversible reduction of the nitro group to a hydroxylamine group. The anodic peak at −0.36 V occurring during the reverse scan is attributed[14,26,27] to the reversible back-oxidation of the –NHOH group to the –NO group according to Eq. (*D*).

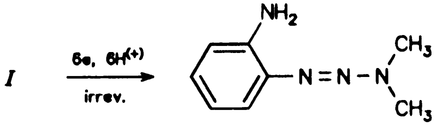
$$\text{Ar–NHOH} \rightleftharpoons \text{Ar–NO} + 2\text{H}^{(+)} + 2e \qquad (D)$$

The reversibility of this process is borne out by the cathodic peak at −0.38 V occurring during the second cycle.

The height of the cathodic peaks in the first cycle is directly proportional to the polarization rate within the region of 10 to 100 mV s^{-1}, irrespective of the pH, which gives evidence that irreversible, diffusion-controlled processes are involved under these conditions.

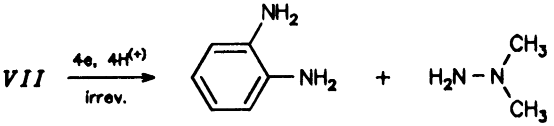
Suggested Reduction Mechanism

The facts described above indicate that at pH 2.0, irreversible six-electron reduction of the nitro group takes place according to Eq. (*E*), followed by four-electron reduction of the triazene group according to Eq. (*F*).



VII

(*E*)

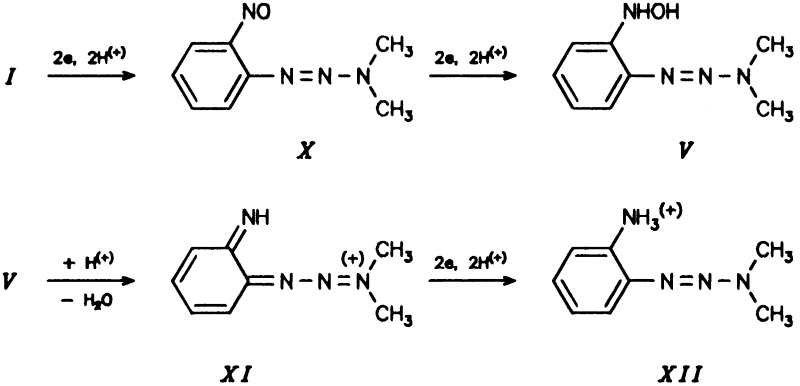


VIII *IX*

(*F*)

The fact that at this pH the decrease of 3rd wave with time is considerably slower for the substance studied than for the unsubstituted triazene[20] and its carboxylamido derivatives[5 – 7] can be ascribed to the stabilizing effect of the nitro group which, owing to its electron acceptor properties, reduces the basicity of the triazene group and, consequently, the rate of its acid-catalyzed hydrolysis according to Eq. (*A*). Still, this hydrolysis plays such a role during the coulometric experiment (that is, in tens of minutes) that the observed number of exchanged electrons is lower than the theoretical value of $n = 10$.

The six-electron reduction of the nitro group apparently proceeds via the ECE mechanism according to Eqs (*G*), which are analogous to the six-electron reduction of *o*-nitroaniline or *o*-nitrophenol[10 – 14,21].

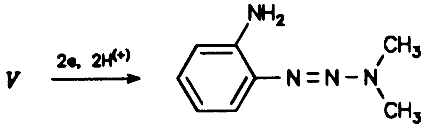


(*G*)

Under these conditions, the quinoid compound *XI* that is formed by the acid catalyzed dehydration is reduced more easily than the hydroxylamine group at the aromatic ring[28,29], owing to which the corresponding wave merges with the wave of reduction of the nitro group. Mesomeric interaction of the triazene group with the hydroxylamine group according to Eq. (*B*) or some of the side reactions that occur during the reduction of phenylhydrazine[29] or nitrobenzene[22], however, are also conceivable.

The rate of formation of the quinonediimonium compound decreases with increasing pH and the hydroxylamine group reduces directly at more negative potentials, which gives rise to two separate waves. Thus, at pH 3 – 6, the first wave can be attributed to the four-electron irreversible reduction of the nitro group to a hydroxylamine group (*V* in Eq. (*G*)), the second wave, to the consecutive reduction of the latter to an amino group following Eq. (*H*),

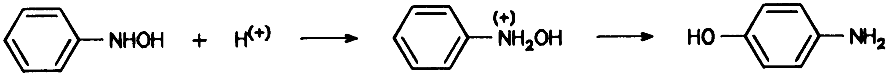
whereas the third wave is due to the reduction of the triazene group according to Eq. (*F*).



VII

(H)

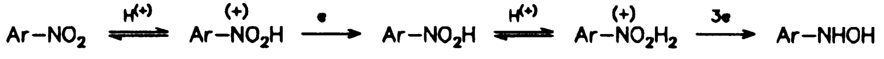
This concept is borne out by the fact that at pH 3 – 6, the half-wave potential of the second wave is about 80 mV more positive than that of the wave of unsubstituted phenylhydroxylamine, which can be ascribed to the –M effect of the triazene group, facilitating the reduction of the –NHOH group. At pH 2, however, the half-wave potential of the second wave shifts abruptly to more positive values and the wave merges with the first wave, whereby the difference from the half-wave potential of phenylhydroxylamine increases in a leap to approximately 250 mV. The only feasible explanation of this leap is in terms of an intermediate reaction according to Eqs (*G*). The fact that the height of the wave appearing at pH 2 as a result of the merging of waves 1 and 2 is directly proportional to the square root of the mercury reservoir height indicates that the above-mentioned intermediate reaction is so fast that the entire process is diffusion-controlled. The observed value of $n = 5.2$ for the region of the limiting current of 2nd wave at pH 5.0 indicates that the reduction according to Eq. (*G*) fails to be completely quantitative, presumably due to the occurrence of side or consecutive reactions[25] such as the acid-catalyzed rearrangement of the hydroxylamine group according to Eq. (*I*),



(*I*)

which lowers the experimental *n* value of aromatic nitro compounds[30] as compared to the theoretically expected value of 6. This is why the observed value of $n = 9.0$ for the limiting current of 3rd wave at pH 5.0 is lower than the theoretically expected value of 10. However, the decomposition of the triazene group during the coulometric experiment, viz. after the stabilizing effect of the nitro group ceases to act, can also play a role.

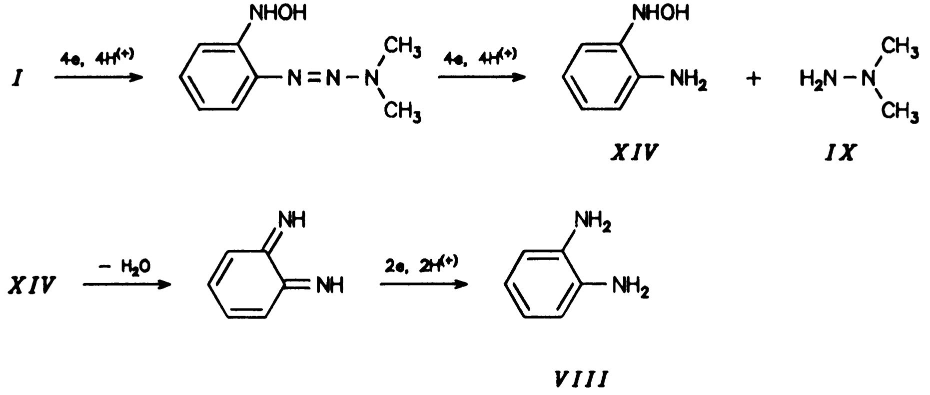
The hydroxylamine group is not reduced further at pH > 7, so that the 1st wave should only correspond to the four-electron reduction of the nitro group. However, the value of $n = 4.6$ obtained by potentiostatic coulometry for the limiting current of the 1st wave at pH 11.1 indicates that the six-electron reduction according to Eqs (*G*) participates to an extent as well, now, however, in basic catalysis conditions as described earlier for *o*-nitrophenol and *o*-nitroaniline[10,21]. The reaction is slower, so that its effect only appears during the coulometric experiment whereas the polarographic wave height corresponds to the exchange of four electrons. The splitting of the 1st wave at pH 8 – 10 apparently corresponds to the case of nitrobenzene in aqueous-alcoholic solutions[31] whose wave splits into a one-electron wave and a three-electron wave due to the slowed-down protonation of the intermediate *XIII* in Eqs (*J*) (ref.[22]).



$$\underset{I}{\text{Ar--NO}_2} \xrightleftharpoons{H^{(+)}} \text{Ar--}\overset{(+)}{\text{N}}\text{O}_2\text{H} \xrightarrow{e} \underset{XIII}{\text{Ar--NO}_2\text{H}} \xrightleftharpoons{H^{(+)}} \text{Ar--}\overset{(+)}{\text{N}}\text{O}_2\text{H}_2 \xrightarrow{3e} \underset{V}{\text{Ar--NHOH}} \qquad (J)$$

Since this splitting is considerably less marked in systems with lower methanol contents, it is reasonable to assume that the surface protonation of intermediate products adsorbed on the electrode surface, whose rate is reduced by the competitive adsorption of molecules of methanol, occurs during the reduction of the nitro group in 1-(2′-nitrophenyl)-3,3-dimethyltriazene as well.

The fact that coulometry at a constant potential of –1.4 V gave a value of $n = 8.7$ at pH 8.0 can be related with the basically catalyzed dehydration following Eqs (*K*).



(*K*)

The observed changes in the shape and height of the 3rd wave, which corresponds to the reduction of the triazene group at pH 7 – 10, can be explained[5 – 8] in terms of the preceding protonation of the triazene groups in the analyte molecules adsorbed on the mercury electrode surface.

Analytical Application of Polarographic Reduction of 1-(2'-Nitrophenyl)-3,3-dimethyltriazene

For tast polarography, the Britton–Robinson buffer–methanol mixture 1 : 1 of a resulting pH of 5 or 11 emerged as optimal from the analytical point of view. In such conditions the dependences of the heights of the observed waves on the analyte concentration are linear across the region of 100 – 2 μmol l^{-1}. The parameters of the calibration plots are given in Table II.

DPP at a conventional DME displays one to three peaks for 1-(2'-nitrophenyl)-3,3-dimethyltriazene, in dependence on pH (Table III); the peaks correspond to waves in tast polarography. The peak heights were measured from the straight lines connecting the side minima. The marked decrease of the 3rd peak at pH < 2 is apparently again associated with the acid-catalyzed hydrolysis of the triazene group. Medium with pH 5 or 11 again emerged as analytically optimal. The parameters of the concentration dependences measured are given in Table II.

The effect of pH on the FSDP voltammograms of the analyte is documented by Fig. 7. The highest and best developed peaks are obtained at pH 5.7. The concentration dependence parameters measured are given in Table II. A mixture of tenfold diluted Britton–Robinson buffer with methanol (9 : 1) is better suited for the concentration region of 0.2 – 1 μmol l^{-1} because the base electrolyte curves are smoother.

Adsorptive Stripping Voltammetry

The FSDPV peak height increases with time elapsed from the formation of the HMDE to the recording of the voltammogram. This fact, which can be explained in terms of adsorptive accumulation of the analyte on the working electrode surface, can be made use of for additional sensitization of the determination. The effects of the time of accumulation, potential of accumulation, buffer concentration, methanol content and stirring

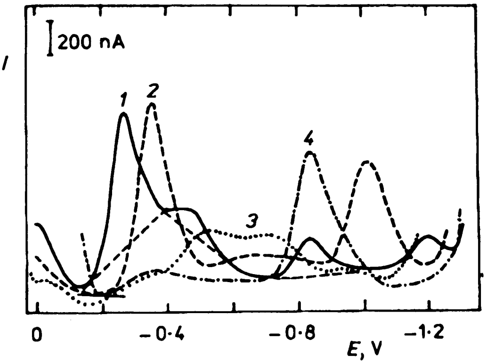


FIG. 7
FSDP voltammograms of 1-(2'-nitrophenyl)-3,3-dimethyltriazene (c = 10 μmol l^{-1}) in Britton–Robinson buffer–methanol mixtures (1 : 1) at pH 3.8 (*1*), 5.7 (*2*), 8.7 (*3*) and 10.9 (*4*). Broken lines are baselines from which the peak height was measured

TABLE II

Calibration curve parameters for polarographic and voltammetric determination of 1-(2′-nitrophenyl)-3,3-dimethyltriazene in Britton–Robinson buffer–methanol mixtures (1 : 1)

Method	pH[a]	c, mol l^{-1}	1st wave or peak				3rd wave or peak			
			slope mA mol^{-1} l	intercept nA	r[b]	L_Q[c] mol l^{-1}	slope mA mol^{-1} l	intercept nA	r[b]	L_Q[c] mol l^{-1}
Tast	5.0	(1 – 10) . 10^{-5}	4.6	-9.0	0.9994	–	4.57	-9.5	0.9998	–
		(2 – 10) . 10^{-6}	4.6	-1.5	0.9998	0.8 . 10^{-6}	4.45	-5.4	0.9997	1.2 . 10^{-6}
	11.1	(1 – 10) . 10^{-5}	5.9	-10.0	0.9996	–	[d]	–	–	–
		(2 – 10) . 10^{-6}	6.0	-1.0	0.9983	1.0 . 10^{-6}	[d]	–	–	–
DPP	5.0	(1 – 10) . 10^{-5}	10.0	-18.0	0.9997	–	8.7	-22.0	0.9996	–
		(1 – 10) . 10^{-6}	8.6	-3.4	0.9993	–	6.5	-4.0	0.9993	–
		(2 – 10) . 10^{-7}	5.0	0.2	0.9975	1.8 . 10^{-7}	3.5	-0.2	0.9934	2.1 . 10^{-7}
	11.1	(1 – 10) . 10^{-5}	8.9	-10.0	0.9999	–	[d]	–	–	–
		(1 – 10) . 10^{-6}	8.6	-0.9	0.9991	–	[d]	–	–	–
		(2 – 10) . 10^{-7}	8.4	-0.2	0.9985	1.2 . 10^{-7}	[d]	–	–	–
FSDPV	5.7	(1 – 10) . 10^{-6}	10.4	0.2	0.9994	5.0 . 10^{-7}	7.6	2.7	0.9962	1.3 . 10^{-6}
FSDPV[e]	5.1	(2 – 10) . 10^{-7}	15.6	0.5	0.9989	0.9 . 10^{-7}	[f]	–	–	–
FSDPV[g]	7.2	(2 – 10) . 10^{-8}	57.5	1.1	0.9989	0.9 . 10^{-8}	[f]	–	–	–

[a] Resulting pH of the mixed medium; [b] correlation coefficient; [c] limit of determination; [d] a single wave or peak is obtained; [e] medium of tenfold diluted Britton–Robinson buffer–methanol mixture 9 : 1; [f] third peak fails to be evaluated due to its coincidence with the current corresponding to the base electrolyte solution; [g] measured with adsorptive accumulation.

were examined with respect to the peak height, and the following conditions were chosen for AdSV: $E_{acc} = 0$ V, $t_{acc} = 30$ s, stirred medium of tenfold diluted Britton–Robinson buffer–methanol (99 : 1) at pH 7.2. The FSDPV record was made 15 s after completed stirring. In such conditions the FSDPV peak height was linearly dependent on analyte concentration across the region of 0.02 – 0.1 μmol l^{-1}. The calibration straight line parameters are given in Table II. The determination cannot be additionally sensitized by extending the time of accumulation because if this time is longer than 30 s, the peak height for the stirred solution decreases, presumably due to a passivation of the working electrode whose surface is not renewed during the measurement.

TABLE III
Effect of pH on the DP polarographic behaviour of 1-(2′-nitrophenyl)-3,3-dimethyltriazene in Britton–Robinson buffer–methanol mixtures (1 : 1)

pH[a]	E_p^1, mV	I_p^1, μA	E_p^2, mV	I_p^2, μA	E_p^3, mV	I_p^3, μA
0.9[b]	–75	1.39	[c]	[c]	–700	0.29
1.9[b]	–150	1.31	[c]	[c]	–725	0.73
2.8	–205	1.09	–350	0.45	–770	0.91
4.0	–285	1.08	–525	0.30	–875	0.92
4.8	–325	1.00	–620	0.20	–935	0.88
5.9	–360	0.96	–750	0.10	–1 025	0.75
7.2	–440	0.65	[c]	[c]	–1 170	0.85
8.0	–490	0.39	[c]	[c]	–1 185	0.54
8.6[e]	–510	0.14	[c]	[c]	–1 185	0.14
	–765	0.42	[c]	[c]		
9.2	–800	0.57	[c]	[c]	–1 190	0.05
10.2	–845	0.78	[c]	[c]	[c]	[c]
11.2	–855	0.89	[c]	[c]	[c]	[c]
12.1	–855	0.89	[c]	[c]	[c]	[c]
13.5	–830	0.95	[c]	[c]	[c]	[c]

[a] Resulting pH of buffer or perchloric acid mixture with methanol; [b] adjusted with 1 M $HClO_4$; [c] 2nd peak fails to be measurable; [d] adjusted with 0.1 M $HClO_4$; [e] 1st peak splits at this pH.

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