

ELECTROCHEMICAL REDUCTION OF BENZENEDIAZONIUM SALTS IN APROTIC MEDIUM

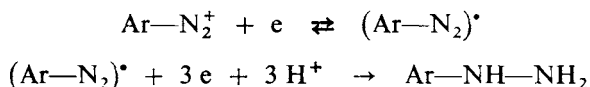
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Received July 5th, 1988
Accepted October 12, 1988

DC polarography, TAST polarography, differential pulse polarography, polarography with superimposed alternating current, slow cyclic voltammetry with a hanging Hg drop electrode and a Pt electrode, rapid cyclic voltammetry with a hanging Hg drop, and coulometry were used to study the electrochemical reduction of *p*-methoxy- and *p*-nitrobenzenediazonium cations in aprotic medium. A reduction mechanism involving two separate one-electron steps is proposed, the first of which being complicated by adsorption and follow-up chemical reaction leading to evolution of nitrogen. The basicity of the aprotic solvents, expressed by donor numbers according to Gutman, influences the reduction mechanism of these cations.

The electrochemical activity of benzenediazonium salts in aqueous media was studied by a number of authors¹⁻¹². The reduction scheme of Wawzonek⁷



is considered as generally accepted. Elofson¹⁰ substantiated by coulometry that the overall reaction involves four electrons and pointed out the splitting of the first reduction wave, which is controlled by diffusion, to two, the first of which has an adsorption character. Orange¹¹ proposed a four-step reduction scheme in acidic aqueous media; this involves both adsorbed and free radicals of benzenediazonium, the formation of diaryl mercury with splitting off of nitrogen, and gradual hydrogenation to phenylhydrazonium cation. Elofson and Gadallah¹³, studying the reduction in sulpholane, found the first reduction step at high positive potentials (up to 0.45 V) and characterized it as a one-electron, diffusion-controlled process. They observed "erratic currents" at more negative potentials, whose origin remained unclear. Also Böttcher¹⁴ studied only the first reduction step of benzenediazonium salts in the medium of nitromethane. Both mentioned works present linear dependences of the half-wave potential of the first reduction wave on the substituent constants, which could not be done for the case of aqueous medium at that time^{15,16}. The formation

of aryl radicals in the first reduction step was made use of by Gadallah¹⁷ in electrochemical arylation of aromatic compounds in acetonitrile.

The aim of the present work is to contribute to the knowledge about the mechanism of electrochemical reduction of benzenediazonium salts in aprotic media.

EXPERIMENTAL

Apparatus and Methods

D.C. polarography: OH-105 type Polarograph (Radelkis, Hungary) with a freely dropping mercury electrode ($m = 3.26 \pm 0.03 \text{ mg s}^{-1}$, $t_k = 2.22 \pm 0.02 \text{ s}$ at a height of mercury column 50 cm on open circuit).

TAST and DPP methods: Apparatus PA 3 (Laboratorní přístroje, Czechoslovakia) with a static mercury drop SMDE 1 (same manufacturer), drop time 2 s; a pulse with an amplitude of -25 mV was applied in DPP, potential sweep rate 2 mV s^{-1} , RC constant 10 ms.

Slow cyclic voltammetry: Apparatus PA 3 with manual switching over of the mode of polarization, potential sweep rate $20\text{--}500 \text{ mV s}^{-1}$, hanging mercury drop (SMDE 1) with $1.320 \pm 0.005 \text{ mm}^2$ surface area, and a platinum disc of $0.57 \pm 0.02 \text{ mm}^2$ surface area.

Rapid cyclic voltammetry: Universal Polarograph PRG 4 (Tacussel, France) with a storage oscilloscope 3 103 N (Tektronik, GB) at sweep rates $0.5\text{--}100 \text{ V s}^{-1}$ and a hanging mercury drop (HMDE 1).

AC polarography: Polarograph OH 105 with a dropping mercury electrode with a controlled drop time 4 s, AC component amplitude 20 mV and frequency 60 Hz.

Coulometry: Either in set-up (1) PA 3 apparatus as a potentiostat with IG6 integrator (Tacussel, France) or in set-up (2) OH 405 potentiostat and UNIT OH 404 integrator (both Radelkis, Hungary), always in the circuit of the auxiliary electrode. The working electrode was a mercury pool, the auxiliary electrode was separated by a glass frit, and the solution was stirred by a stream of nitrogen. The decrease of the depolarizer content was followed polarographically.

The base electrolyte was 0.1M-NaClO_4 in all cases. A three-electrode system was used with a Pt counter-electrode and AgCl reference electrode separated from the electrolysis compartment by a salt bridge with a Luggin capillary filled with the base electrolyte. The potential of the working electrode was measured with a millivoltmeter MV-870 (Präcitronik, G.D.R.). The potential values given below are referred to the saturated calomel electrode.

To prevent decomposition of the diazonium salts, the electrolytic cell was immersed in a mixture of water and ice. Measurements at variable temperature were carried out in a cell with a thermostated mantle-piece connected with a cryostat MK-70 (G.D.R.).

EPR spectra were recorded on a spectrometer ER 9 (Zeiss, G.D.R.) by the method of internal electrochemical radical generation in the resonator cavity¹⁸.

Elementary analysis was made on a CHN Analyser (Carlo Erba, Italy) with an accuracy of $\pm 1\%$ for carbon, $\pm 0.3\%$ for nitrogen, and $\pm 0.1\%$ for hydrogen.

Chemicals

Diazonium salts were prepared by direct diazotation¹⁹ of primary *p*-substituted aniline suspended in a solution of HF and H_3BO_3 with a solution of NaNO_2 in the stoichiometric ratio during

cooling so that the temperature did not rise above -10°C . The crystals of tetrafluoroborate of the *p*-substituted diazonium salt were immediately sucked off, washed with cold diethyl ether, and then precipitated from acetone solution three times with diethyl ether. The products were stored in an exsiccator at a low temperature. The presence of a primary amine or phenol and azo compounds was tested by means of thin-layer chromatography on Silufol (Kavalier, Czechoslovakia) with mobile phase benzene-methanol (4 : 1).

Electrochemical reduction was studied with *p*-methoxybenzenediazonium (*I*) and *p*-nitrobenzenediazonium tetrafluoroborate (*II*).

Elementary analysis: *I*, found 37.18% C, 3.20% H, 12.49% N; calculated 37.88% C, 3.18% H, 12.62% N; *II*, found 30.50% C, 1.79% H, 17.66% N; calculated 30.42% C, 1.70% H, 17.74% N. Both compounds are sufficiently thermally stable; *I* represents derivatives with a typical electron donor substituent, *II* derivatives with a typical electron acceptor substituent and moreover it permits electrochemically to study the properties of the reduction products of the electroactive nitro group.

RESULTS AND DISCUSSION

Polarography

TAST-polarographic curves of *I* in dimethylformamide (DMF) can be characterized by the current, i_1 , at relatively higher positive potentials; with *II*, this reduction wave is shifted close to the potential of mercury anodic dissolution. Further there is a characteristic wave at about 0 V with a limiting current i_2 , and at potentials from -0.5 to -1 V "erratic" currents (Fig. 1), which at diazonium salt concentrations higher than about $4 \cdot 10^{-4} \text{ mol l}^{-1}$ exceed the current i_2 several times. At higher negative potentials, *II* gives a reduction wave due to the nitro group. The dependence of the currents i_1 , i_2 and their sum on the concentration corresponds to the model with an adsorption prewave (Fig. 2). This is in accord with the dependences of i_1 and i_2 on the height of mercury column in DC polarography using non-regulated dropping mercury electrode. The slope of the dependence of $\ln i_1$ on $\ln h_{\text{Hg}}$ (h_{Hg} denotes height of mercury column) is close to unity (0.986) and the slope of the dependence of $\ln(i_1 + i_2)$ on $\ln h_{\text{Hg}}$ is close to 0.5 (0.496). Since the sum of $i_1 + i_2$ is controlled by diffusion, the logarithmic analysis was done by plotting $\log [i/((i_1 + i_2)_L - i)]$ against $(n/0.054) E$ (at 0°C). This gave the numbers of transferred electrons in the particular waves $n_1 = n_2 = 1$ for *I*, $n_2 = 1$ for *II* (n_1 cannot be determined), and the half-wave potentials $E_{1/2}^{(1)} = 0.115 \text{ V}$ and $E_{1/2}^{(2)} = 0.033 \text{ V}$ for *I*, $E_{1/2}^{(2)} = 0.090 \text{ V}$ for *II* ($E_{1/2}^{(1)}$ is more positive than 0.3 V).

The diffusion coefficients of both derivatives in DMF were calculated from the concentration dependences of $i_1 + i_2$ and recalculated to 25°C according to the equation $D_t = D_0(1 + \alpha \Delta t/100)$ (D_t and D_0 denote diffusion coefficients at t and 0°C , $\alpha = 3\% \text{ K}^{-1}$ (ref.²⁰)). The results for the compounds *I* and *II* are: $D(I) = (2.9 \pm 0.3) \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $D(II) = (3.5 \pm 0.3) \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The DPP curves are similar in character to the corresponding TAST polarographic curves (Figs 3 and 4). The width at half peak height of p_2 corresponds to the theoret-

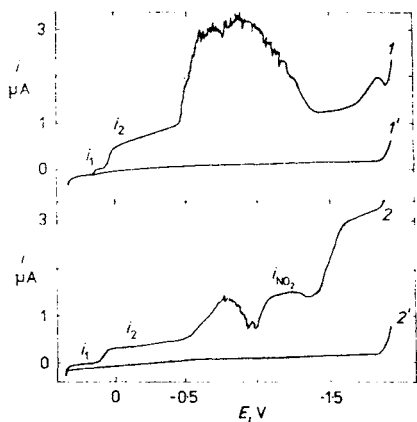


FIG. 1
TAST polarographic curves for compounds *I* and *II* in DMF at 0°C. 1 $c_I = 5.60 \cdot 10^{-4} \text{ mol l}^{-1}$; 1' base electrolyte ($0.1 \text{ mol} \cdot \text{l}^{-1} \text{ NaClO}_4$). 2 $c_{II} = 3.20 \cdot 10^{-4} \text{ mol l}^{-1}$; 2' as 1'

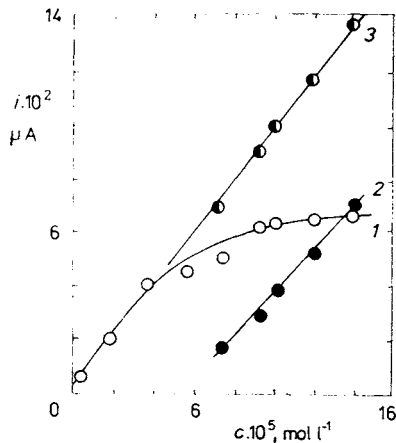


FIG. 2
Concentration dependence of polarographic limiting currents. 1 i_1 ; 2 i_2 ; 3 $i_1 + i_2$. Compound *I*, TAST polarography in DMF at 0°C

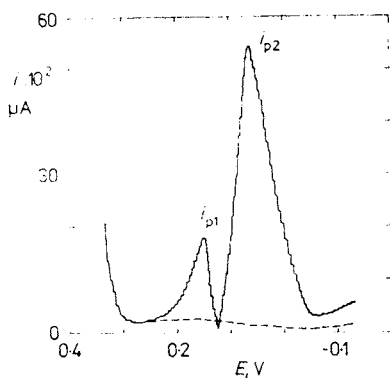


FIG. 3
DPP curve for *I* in DMF ($5.05 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$) at 0°C. $E = -25 \text{ mV}$, $\nu = 2 \text{ mv s}^{-1}$ (solid line); dashed line corresponds to base electrolyte

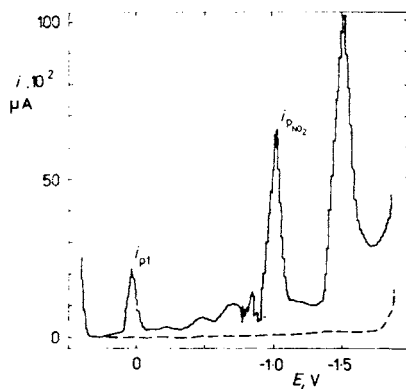


FIG. 4
DPP curve for $4.10 \cdot 10^{-4} \text{ mol l}^{-1}$ *II* in DMF. Other data as in Fig. 3

tical value 85.6 mV at the given amplitude of the superimposed pulse ΔE , drop time and temperature, assuming one-electron diffusion process. This is in accord with the comparison of the TAST polarographic and DPP peak currents. This ratio was expressed for I and a stationary electrode by the ratio of the slopes of the concentration dependences of $i_1 + i_2$. The obtained value, 1.22 ± 0.03 , is in good agreement with the theoretical value for a one-electron process²¹, 1.251.

Cyclic Voltammetry

At polarization rates up to 500 mV s^{-1} on a hanging mercury drop and at low concentrations (Fig. 5) a cathodic and a corresponding anodic peak can be seen on the curves. These are in the ratio of $i_{pa1}/i_{pk1} = 1$. At potentials more negative than -0.8 V , erratic currents are observable on the curves. At concentrations of the diazonium salt higher than $2 \cdot 10^{-4} \text{ mol l}^{-1}$, the cathodic peak near to 0 V doubles and the anodic branch becomes deformed (Fig. 5). The existence of a redox peak of the NO_2 group at about -1.1 V on the curves for II suggests that the electrode surface is not blocked with respect to further electron transfer.

The characteristics and criteria given in Tables I and II are in accord with the EC mechanism^{23,24} assuming a one-electron transfer. However, the kinetics of the follow-up chemical reaction cannot be determined with certainty. Measurements of cyclic curves for I at various temperatures from -17 to $+15^\circ\text{C}$ at a concentration chosen such that the values of i_{pk1} and i_{pk2} were comparable with each other led to

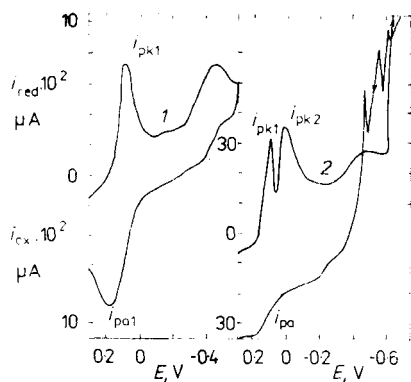


FIG. 5

Typical cyclic voltammograms for I in DMF on a hanging mercury drop at 0°C . 1 $7.66 \cdot 10^{-5} \text{ mol l}^{-1}$, $\nu = 20 \text{ mV s}^{-1}$; 2 $3.68 \cdot 10^{-4} \text{ mol l}^{-1}$, $\nu = 100 \text{ mV s}^{-1}$

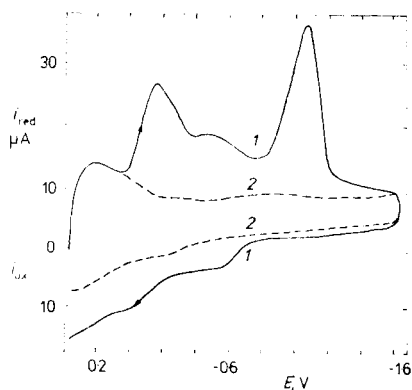


FIG. 6

Cyclic voltammogram for $7.25 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1} I$ in DMF on a hanging mercury drop at 0°C , $\nu = 100 \text{ V s}^{-1}$. 1 Base electrolyte with I ; 2 base electrolyte only

the determination of the dependence of the current on the temperature. The slope of the $\ln i - T$ dependence gave the temperature coefficient $\omega = (di/i dT) \cdot 100$ ($\% K^{-1}$). Thus, we have $\omega = 1.7$ for i_{pk1} and T higher than 268 K, $\omega = 1.4$ for i_{pk2} and $\omega = 1.8$ for i_{pa2} . These values correspond to diffusion processes. The non-linear dependence of $\ln i_{pk1}$ on T can be attributed to two concurrent processes with different temperature coefficients, electron transfer and adsorption. The magnitude of the erratic currents decreases with decreasing temperature. Higher polarization rates (more than $1 V s^{-1}$) result in: (i) an increase of i_{pk1} (the slope of the dependence of $\ln i_{pk1}$ on $\ln v$ is equal to 0.5) and a shift to more negative potentials, (ii) peak p_{k2} ceasing to increase at $v > 5 V s^{-1}$ until both cathodic peaks fuse to one (at $v > 20 V \cdot s^{-1}$) totally irreversible peak, while peak p_{a2} diminishes, and (iii) a decrease of the erratic currents, while at $v > 50 V s^{-1}$ the compound I gives a single totally irreversible peak in the potential range from -1.0 to $-1.3 V$ (Fig. 6).

These changes can be elucidated by the fact that the adsorption equilibrium is not attained at the high polarization rates indicated. The reduction peak at $-1.05 V$

TABLE I
Diagnostic criteria of cyclic voltammetric curves for I in DMF on a mercury drop

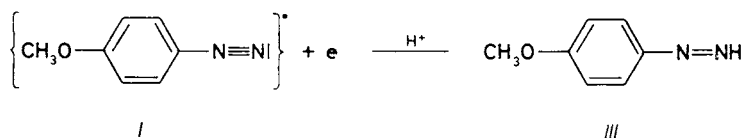
Current	$i = f(c)$	x^a	$dE/d \log c$	$dE/d \log v$
i_{pk1}	nonlinear	0.44 ± 0.02	$33 \pm 5 \text{ mV}$	$-34 \pm 5 \text{ mV}$
i_{pk2}	$i = kc + q$	0.42 ± 0.02	0	$-31 \pm 5 \text{ mV}$
i_{pa1}	nonlinear	0.64 ± 0.03	0	0
i_{pa2}	$i = kc + q$	0.26 ± 0.03	0	0

^a Coefficient of the dependence of peak current on polarization rate.

TABLE II
Characteristics of the peak form for I in DMF on a mercury drop. Data for anodic peaks are not given since these peaks are not well distinguished

Current	$E_p - E_{p/2}$
i_{pk1}	$54 \pm 2 \text{ mV}$ for $c \cdot 10^{-4} \text{ mol l}^{-1}$ $38 \pm 2 \text{ mV}$ for $c \cdot 10^{-4} \text{ mol l}^{-1}$
i_{pk2}	$46 \pm 2 \text{ mV}$

could correspond to second one-electron transfer with subsequent formation of benzodiimide (*III*), whose existence is assumed by Lahoti²⁵ (Scheme 1). This mecha-



SCHEME 1

nism could elucidate the gradual disappearance of the anodic peak p_{a2} at increasing polarization rates. Similarly, the lowering of the erratic currents with increasing polarization rate can be attributed to decreasing contribution of the reaction involving splitting of the C—N bond with the evolution of nitrogen gas.

The use of the platinum electrode permitted to broaden the working range of potentials to 0.75 V. Both compounds under study give two cathodic current signals on a Pt electrode at 0 V, similar to those on a mercury drop (Fig. 7). (Table III). The reduction potential of the NO₂ group in *II* corresponds to that of the NO₂ group in nitrobenzene under the same conditions. This is substantiated by the mechanism of splitting of the C—N bond with the evolution of gaseous nitrogen. However, this reaction is not manifested by erratic currents on a solid electrode. A comparison of the reductions on Hg and Pt electrodes revealed that the adsorption is not selective with respect to the cathode material, hence it is not related with the formation of phenylmercury compounds.

Polarography With Superimposed Alternating Current (A.C. Polarography)

The use of AC polarography served us to separate adsorption and faradaic currents. The concentration dependence of AC current for compound *I* was measured at -20°C and the temperature dependence in the range from -20 to +10°C. The only pronounced peak is formed close to -0.1 V at temperatures below 0°C and concentrations higher than $3 \cdot 10^{-4} \text{ mol l}^{-1}$; it has an adsorption character and diminishes with rising temperature. Its concentration dependence (Fig. 8) corresponds to the model of adsorption of the reduced form of *I*.

Macroelectrolysis

To determine the number of electrons transferred per one molecule of *I*, coulometric electrolysis was carried out with a mercury pool electrode at four potentials: +0.100 V, i.e. at the adsorption prewave, -0.150 V, i.e. at the limiting polarographic current i_2 , -0.850 V, i.e. in the middle of the region of erratic currents, and at -1.650 V, i.e. beyond this region. The results are summarized in Table IV.

If we do not consider the possibility of a loss of *I* during analysis by thermal decomposition (this was carefully checked), the consumption of one electron per one molecule of *I* during electrolysis at -1.650 V can be attributed to recombination of radicals, which may be either primary or secondary (phenyl). This, however, does not elucidate the markedly lower electron consumption at potentials more positive than -0.850 V. In electrolysis of a stirred solution, in contrast to electrolysis on a dropping mercury electrode, we have to consider the follow-up reaction of the

TABLE III
Characteristics of cyclic voltammetric curves for *I* and *II* in DMF on a platinum disc

Compound	E_{pk1}^a , V	E_{pk2}^a , V	x_2^b	x_1^b
<i>I</i>	-0.115	-0.475	0.75	0.35
<i>II</i>	0.315	-0.405	0.75	0.44

^a For $c \approx 7 \cdot 10^{-4} \text{ mol l}^{-1}$ and polarization rate 100 mV s^{-1} ; ^b coefficient of the dependence of peak current on the polarization rate; $c \approx 7 \cdot 10^{-4} \text{ mol l}^{-1}$ (for $c < 3 \cdot 10^{-4} \text{ mol l}^{-1}$ is $x_1 = 0.45$, and increases with the concentration up to 0.9).

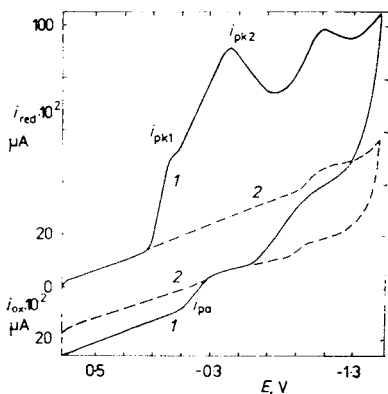


FIG. 7

Cyclic voltammogram for $7.33 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ *I* in DMF on a Pt disc. 1 Base electrolyte with *I*, 100 mV s^{-1} , 0°C ; 2 base electrolyte

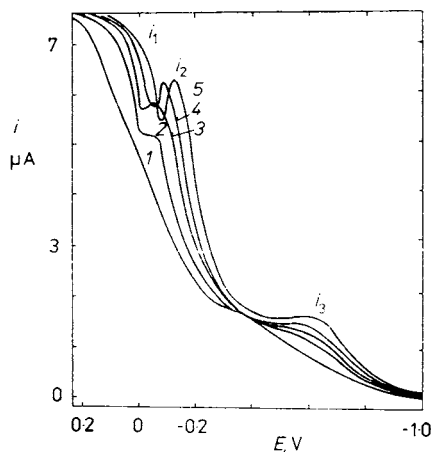
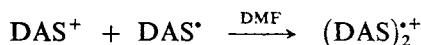


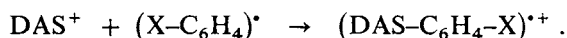
FIG. 8

AC polarographic curves for *I* in DMF at -20°C . Concentration of *I*: 1 zero; 2 $1.50 \cdot 10^{-4} \text{ mol l}^{-1}$; 3 $3.36 \cdot 10^{-4} \text{ mol l}^{-1}$; 4 $5.91 \cdot 10^{-4} \text{ mol l}^{-1}$; 5 $9.60 \cdot 10^{-4} \text{ mol l}^{-1}$

primary diazonium salt radical, DAS^\bullet , or splitting off of nitrogen from the formed secondary radical with another DAS^+ cation with the participation of the solvent:



or



The two reactions do not exclude the acceptance of another electron at a higher negative potential. Thus, the first step involves one electron per two molecules of *I* and the second two electrons per two molecules. Detection of the primary diazonium radical or the secondary phenyl radical by ESR spectroscopy was unsuccessful.

However, internal electrochemical generation of radicals in the resonatorcavity¹⁸ served us to prove the existence of an intermediate radical product of electrochemical reduction of the NO_2 group in *II*. The character of the recorded spectrum corresponds unambiguously to the ESR spectrum of the anion radical of nitrobenzene²⁶ including splitting of the lines due to hydrogen in *para* position (i.e. in place of the diazonium group originally present). This substantiates the mechanism of splitting of the C—N bond and evolution of nitrogen gas.

As shown earlier²⁷, the reduction in acetone medium has a somewhat different character than in DMF. We therefore selected further polar solvents, acetonitrile from the group of "acidic" (according to Gutman²⁸) and dimethylsulphoxide in addition to DMF from the group of "basic" solvents. Both derivatives, *I* and *II*, were studied in all four solvents by TAST polarography at concentrations from 1 to $8 \cdot 10^{-4} \text{ mol l}^{-1}$ (Fig. 9). The main characteristics are summarized in Table V together with some literature data. The observed effects, especially suppression of erratic currents can be discussed in terms of various stabilization levels of the solvents of different basicity with respect to the primary and secondary intermediate products, and in terms of different degrees of solvation of the diazonium cation. Its strong

TABLE IV

Number of electrons transferred, *n*, per one molecule of *I* found by coulometry in DMF

Potential, V	<i>n</i>
+0.100	0
-0.150	0.5 ± 0.03
-0.850	0.78 ± 0.05
-1.650	1.0 ± 0.1

solvation is documented by comparing the polarographic diffusion coefficients, whose values in water and in DMF are in the ratio of $D_{\text{DMF}}/D_{\text{Aq}} = 0.41$ on the average, whereas the viscosity ratio is $\eta_{\text{Aq}}/\eta_{\text{DMF}} = 1.1$. On replacing DMF by acetone, we obtain $D_{\text{Ac}}/D_{\text{Aq}} = 2.2$ and $\eta_{\text{Aq}}/\eta_{\text{Ac}} = 2.9$. The number 0.41 is close to the ratio of the polarographic diffusion coefficients for the redox system Eu(III)/Eu(II) in DMF and in water:³⁰ $D_{\text{DMF}}/D_{\text{Aq}} = 0.51$. For phenothiazin, a molecule of about the same size as DAS, but uncharged, the polarographic diffusion coefficients ac-

TABLE V

Characteristics of polarographic reduction of compounds *I* and *II* in aprotic solvents

Solvent	ϵ^a	DN ^b	Prewave	Maximum width, V	n_1^c	n_2^d
DMSO	47	29.8	yes	-0.3 to -1.2	1	2
DMF	37	26.6	yes	-0.5 to -1.3	0.5	1
Acetone	22	17.0	no	-1.0 to -1.6	1	2
AN	38	14.1	no	-1.2 to -1.7	1	2
Sulpholane ^f	35	14.8	no	-0.5 to -1.0	1 ^e	—
CH ₃ NO ₂ ^g	43	2.7	no	—	—	—
Water ^h	80	30	yes	<i>i</i>	1	4 ⁱ

^a Relative permittivity; ^b donor number, ref.²⁸; ^{c,d} number of electrons transferred per one DAS molecule, found by coulometry; ^e found by comparison of the wave height with the reduction wave for benzophenone; ^f ref.¹³; ^g ref.¹⁴; ^h ref.¹¹; ⁱ another reduction mechanism.

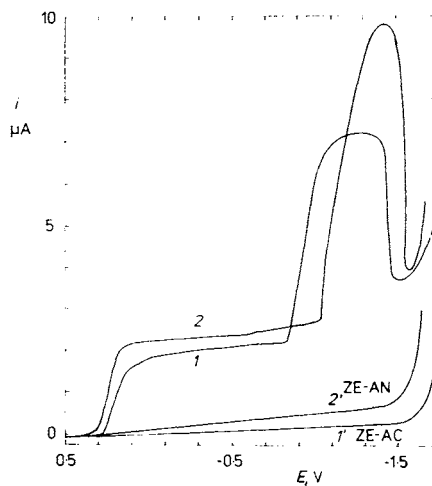
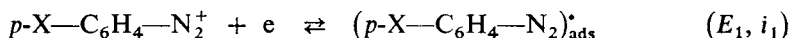


FIG. 9

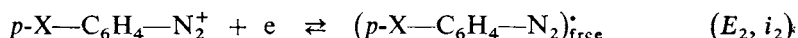
TAST polarographic curves for *I*. 1 Acetone, $5.83 \cdot 10^{-4} \text{ mol l}^{-1}$; 1' base electrolyte ($0.1 \text{ mol l}^{-1} \text{ NaClO}_4$ in acetone); 2 acetonitrile, $8.18 \cdot 10^{-4} \text{ mol l}^{-1}$; 2' base electrolyte ($0.1 \text{ mol l}^{-1} \text{ NaClO}_4$ in acetonitrile). 0°C , $\nu = 2 \text{ mV s}^{-1}$

ording to Opallo³⁰ are $D_{Ac} = 17.3 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_{DMF} = 10.3 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. In the medium of acetone, the polarographic diffusion coefficient of I is $D_{Ac} = 19.6 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. In DMF, however, the diffusion coefficient is much smaller, $4 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This may be attributed to solvation of the cation by the basic solvent. The influence of the solvent is more complicated in certain steps of electroreduction as discussed below.

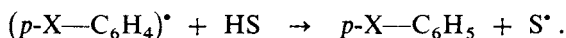
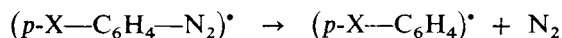
Based on the above findings, the following scheme of electroreduction of benzenediazonium salts in nonaqueous media is proposed: At low concentrations of DAS (below $2 \cdot 10^{-4} \text{ mol l}^{-1}$)



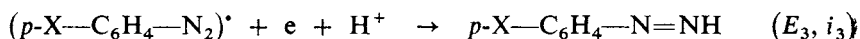
at higher concentrations of DAS (more than $4 \cdot 10^{-4} \text{ mol l}^{-1}$) on the covered electrode surface



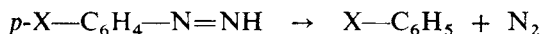
with follow-up reactions



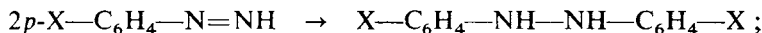
Both these reactions are concurrent with the possible second reduction step



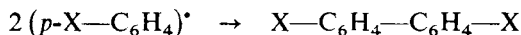
with possible follow-up reactions



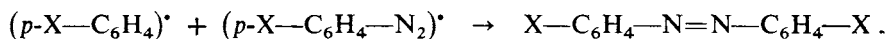
or



even recombination of radicals cannot be excluded:



and to a lesser extent



Adsorption is significant only in basic aprotic solvents. Peculiarities of the reduction mechanism in DMF during coulometric electrolysis in a stirred solution were dis-

cussed above. The erratic currents in the region from -0.5 to -1.5 V (according to basicity of the solvent) are probably due to evolution of nitrogen bubbles. The basicity of the solvent also influences the division of the first reduction step into two peaks; this effect was insensitive to the cathode material, and it can be attributed to blocking of the electrode surface by the adsorbed reduced form of the depolarizer. This results in a hindrance of the reduction of further depolarizer molecules, transported by diffusion. Further reduction can proceed only at a sufficiently high negative potential.

The authors are indebted to Prof. O. Fischer for continuous attention and valuable advices.

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Translated by K. Micka.