ELECTROCHEMICAL REDUCTION OF 2,2'-DINITRODIPHENYL ETHER AND 2,2'-DINITRODIPHENYLAMINE AT MERCURY CATHODES

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2,2'-Dinitrodiphenyl ether (*I*) is reduced at less negative potentials than 2,2'-dinitrodiphenylamine (*II*); the respective mechanisms of their reduction differ essentially. (*I*) is electrolytically reduced in a single wave with an uptake of eight electrons per molecule, giving rise to a bishydroxylamine intermediate which undergoes an intramolecular disproportionation. The resulting 2-nitroso--2'-amino-diphenyl ether undergoes a chemical follow-up reaction leading on the one hand to dibenzo-(*b,e*)-(1,4,5)-oxadiazepine, on the other hand to a diphenylamine product (resulting by a chemical rearrangement) which reacts with reductants present in the solution and yields dihydrophenazine.

It is merely by chance that in the electrolytical reduction of *II* dihydrophenazine also results in addition to other products. 2,2'-dinitrodiphenylamine (*II* enables here, however, a partial electrolytical reduction in which 2-amino-2'-nitrodiphenylamine is formed in a single 6-electron wave. In the following, more negative wave, is clearly separated only in alkaline media, the other nitro group reduces with an uptake of 4 electrons to an intermediate which eliminates the hydroxylamine group with the corresponding electron pair. The subsequent chemical reaction leads to dihydrophenazine. This substance is the reduced form of an chemically and electrochemically reversible system, this system participates in the chemical reactions of reaction intermediates. Its regeneration readily proceeds at potentials more positive than the reduction potential of *II*. Phenazine is oxidized in the catholyte by the hydroxylamine set free to phenazine N-oxide. Nitrogen is thus eliminated in its elemental form *via* hydroxylamine from the substrate molecule.

The system 2,2'-dinitrodiphenyl–X, where X may be S, O, NH, CO or CH$_2$ — has been chosen for a systematic investigation of an intramolecular cyclization reaction induced by an antecedent electrolytical reduction. In a preceeding communication[1] we described such a reaction with 2,2'-dinitrodiphenyl sulfide; quite promising results were obtained here. In this communication we intend to support on extending our investigation on 2,2'-dinitrodiphenyl ether (*I*) and 2,2'-dinitrodiphenylamine (*II*). In addition to the main aim, *i.e.* the investigation of the chemical follow-up reaction after electrolysis (this process has to lead preferently to the formation of a 7-membered heterocyclic ring between the benzene nuclei), attention was paid to a partial electrochemical reduction of the starting symmetrical dinitro compound.

As follows from the literature the chemical reductions of *I* and *II* were performed with the use of a considerable numbers of reductants. With *I* mainly 2,2'-diaminodiphenyl ether[2], dibenzo-

[*b,e*]-(1,4,5)-oxadiazepine (*V*) and its dihydro derivative (*VI*), further its 5-oxide[3,4] and phenazine[3] (*XII*)[4] were isolated as products. The substance (*II*) gave a 2-nitro-2′-amine (*XIII*) (ref.[4]), dibenzo[*b,e*]-(1,4,5)triazepine[5], phenazine (*XII*) (ref.[6,7]) and 2,2′-diaminodiphenylamine *XVI*). Accordingly, the partial reduction of *II* by alkaline Na_2S in alcoholic media proceeded with a considerable success.

We further attempted to find out the influence of an exchangn of NH for O in the X joining the two nitrophenyl moieties. In the final communication of this series we are going to describe the behaviour of the two analogues with X = $>$CO and $>$CH$_2$.

EXPERIMENTAL

In the electrochemical investigations the instrumentation and techniques described in our preceding papers[1] were used. The solvents and chemicals used for preparing buffers or made use of as supporting electrolytes were analytical grade reagents. 2,2′-dinitrodiphenylamine (*II*) was prepared according to a procedure published by Eckert and Steiner[8]. The reaction mixture, however, was processed in a different manner from that described in the above communication. It was first extracted with dioxane and the black solution was drawn through a silica gel column. According to TLC tests the filtrate still contained a certain amount of the unchanged starting material. The residue (8 g) after evaporating off dioxane in a rotating vacuum evaporator was redissolved in dichloromethane and separated on a poured chromatographic column (about 200 g of silica gel L Lachema, the diameter of the tube 28 mm) prepared with benzene. The elution was performed first with pure benzene, later with benzene containing 20% (by vol.) CH_2Cl_2. After two preparative column separations pure 2,2′-dinitrodiphenylamine (*II*) resulted, melting at 169·5—170°C. According to the data in the literature 169°C is stated for the m.p. The recommended crystallization from acetic acid or the removing of residues of the non-reacted starting material by distillation causes decomposition.

2-Nitro-2′-aminodiphenylamine was prepared by reduction with alkaline polysulphide in a mixture of water with ethanol. This modified method of a partial reduction of aromatic dinitro compounds yielded a product melting at 105·5—106°C (as compared to 106—107°C in the literature[4]). The attempts to prepare dibenzo[*b,e*]-(1,4,5)-triazepine by a method published[4,5] for the reduction of *II* were without any success. The main products were phenazine (*XII*) and phenazine N-oxide (*XVII*). Phenazine N-oxide purified by chromatography (silica gel L–benzene with 2·5% (by vol.) CH_3COOH) melts with a strong sublimation at 222—222·5°C (sealed capillary).

2,2′-Dinitrodiphenyl ether (*I*) was prepared according to a procedure described in[8].

The samples of substances for elemental analysis and spectral measurements were dried in a desiccator over phosphorus pentoxide *in vacuo* (oil vacuum pump). The melting points quoted here have not been corrected.

RESULTS

2,2′-DINITRODIPHENYL ETHER

Polarographic and Voltammetric Measurements

2,2′-Dinitrodiphenyl ether (*I*) gives two cathodic d.c. polarographic waves with a 4 : 1 ratio of limiting currents in acid supporting electrolytes (pH 0·8 to 5·0), *i.e.*

in acids or in buffers, both containing 50% (by vol.) ethanol. The clearest separation of both waves can be observed at $3.5 < pH < 4.7$. In the neutral and alkaline regions only the more positive wave remains on the polarogram and its height is pH-independent. At pH > 8 $E_{1/2}$ is not function of pH (Fig. 1). Up to this value the slope $\Delta E_{1/2}/\Delta pH$ equals $- 0.87V/pH$. The observed waves are irreversible, diffusion-controlled and concentration-dependent (i_d = const. C).

The curves obtained with a stationary hanging mercury drop electrode exhibit a well-developed cathodic peak (its $E_{p/2}$ corresponds to $E_{1/2}$ on the d.c. polarogram). The commutated curves recorded with the Kalousek circuit (E_{aux} corresponding to the potential of the limiting current of the more positive cathodic wave) give rise to an anodic wave $E_{1/2}$ of which shifts to less negative values with increasing pH. This wave corresponds to the oxidation of hydroxylamine groups formed by reduction of nitro groups in I during the generation cycle at E_{aux}. Cp-Coulometric measurements with a large area mercury cathode (A = 1 cm^2) performed at different pH-values and E gave values of n shown in Table 1.

In microelectrolysis at constant potential (cp-electrolysis) a colouration of the solution often results if the reduction takes place at the potential of the first wave and pH < 4.6. An anodic wave only appears if the electrolysis is performed at pH > > 2.8. This anodic wave increases during electrolysis carried out at pH 4.6 and attains its maximum value towards the end of the electrolysis at the potential of the first wave. On the whole this is the highest value of the limiting current of this anodic wave to be attained during electrolysis. — The height of the more negative cathodic wave remains unchanged during reduction at the above potential. In electrolyses in

TABLE 1

cp-Microcoulometry of 2,2'-dinitrodiphenyl oxide (I) in solutions with 50% (by vol.) ethanol. A at the potential of the more positive wave; B at the potential of the more negative wave

pH	Solution	Number of electrons	
		A	B
0.9	0.5M-H$_2$SO$_4$	9.2	11.0
2.8	Britton–Robinson	9.5	11.8
4.6	buffer	8.5	10.3
6.9	buffer	9.1	—
7.15	buffer	10.4	—
10.25	buffer	10.4	—
12.4	0.2M-NaOH	12.1	—

alkaline solutions up to pH 10·5 but a small anodic wave results during the experiment, the height of which decreases during the electrolysis. In microelectrolysis in 0·2M--NaOH the original cathodic wave decreases with time and a new one forms at $-1·42$ V vs M.S.E. The colour of the solution turns brown and no anodic wave has been observed.

Preparative cp-Electrolysis

The composition of the solutions and the n values in preparative electrolyses of substance *I* at a mercury electrode at different pH values are demonstrated in Table II.

TABLE II

Products and cp-coulometric results from the preparative electrolysis 2,2'-dinitrodiphenyl ether (*I*)
(50% (by vol.) ethanol)

pH	Solution	TLC analysis of the mixture of products after electrolysis	Number of electrons n from the total charge consumption
0·9	0·5M-H₂SO₄	2,2'-diamino-4-hydroxy-diphenyl ether (*IX*)	—
	0·1M-HCl	phenazine (*XII*) oxadiazepine (*V*)	[a]
4·0	Britton–Robinson buffer	phenazine (*XII*) oxadiazepine (*V*) 2,2'-diamino-4-hydroxy--diphenyl ether (*IX*)	11·4
6·8	KH₂PO₄/NaOH	phenazine (*XII*) 2,2'-diamino-4-hydroxy-diphenyl ether (*IX*)	13·2
8·9	KH₂PO₄/NaOH	phenazine (*XII*) oxadiazepine (*V*)	12·9
	0·2M-NaOH	phenazine (*XII*) oxadiazepine (*V*)	13·4
	0·5M-LiCl (in anhydrous ethanol)	oxadiazepine (*V*) non-identified impurities	13·1

[a] The overconsumption does not correspond to the electrolysis.

A typical example is the experiment carried out with $2.5 \cdot 10^{-3}$ mol l^{-1} I in a buffer (KH_2PO_4-NaOH with 50% (by vol.) C_2H_5OH). Immediately at the beginning of the electrolysis the catholyte started to turn yellow, orange and finally purple. The polarograms recorded during electrolysis showed decreasing cathodic waves and a newly formed anodic wave. Towards the end of electrolysis the catholyte exhibited only the small anodic wave and a low cathodic wave with a pH different from that of the starting material I; Its pH was between 7·5 and 8·0. This catholyte was directly extracted with $CHCl_3$. The collected extracts were dried with calcium chloride, $CHCl_3$ was evaporated, and 150 mg of a reddish-brown substance resulted, melting at 124°C with a strong sublimation. The composition of this mixtures of products is shown in Table II. During electrolysis of I in acid media the colour of the catholyte turns orange and finally yellow. Both with 0·5M-H_2SO_4 and at pH 4·0 an anodic wave appears during electrolysis whereas two smaller anodic waves are formed and a crimson colouration results with neutral and alkaline solutions.

Substances Isolated as Products of Preparative Electrolysis

From the mixture of products after electrolysis (Table II) dibenzo[b, e]-(1,4,5)--oxadiazepine (V) has been isolated. The substance was separated from the other products by chromatography of the mixture on a poured silica gel column (benzene--ethyl acetate up to 50% by vol.) giving rise to orange-coloured fractions; on evaporation an orange coloured oily substance was obtained. This product was placed in a refrigerator. This operation yielded crystals melting at 44°C. After recrystallization from light petroleum (b.p. 60−70°C) a substance resulted which exhibited a melting point of 56−57°C (57°C can be found in the literature). The optimum yield was about 18% (in 0·1M-LiCl/C_2H_5OH). The elemental analysis of the product for which a dibenzooxadiazepine structure is assumed (V) is as follows: calculated: for $C_{12}H_8$ . . N_2O (m.w. 196·21): 73·45% C, 4·1% H, 14·21% N; found: 73·40% C, 4·44% H, 14·02% N.

Its IR spectra in $CHCl_3$ exhibited the following characteristic vibration bands: 3 000 cm^{-1} (w), 1 600 cm^{-1} (s), 1 505 cm^{-1} (m), 1 470 cm^{-1} (s), 1 460 cm^{-1} (s), 1 270 cm^{-1} (s).

Over the whole pH range this substance gives a reversible diffusion-controlled cathodic 2-electron wave (in solutions containing 50% (by vol.) ethanol. With the technique of discontinuously changed square-wave voltage (Kalousek commutator) the corresponding anodic wave is obtained. The plot of $E_{1/2}$ *vs* pH of the cathodic waves of the isolated substance is demonstrated in Fig. 1. The slope $\Delta E_{1/2}/\Delta$ pH is -0.065V/pH.

The above spectral data and both physical and polarographic properties confirm attribution of the dibenzooxadiazepine (V) to the described product. Its reduced form, dihydrodibenzooxadiazepine (VI) rapidly and easily oxidizes if exposed to air.

With respect to the more positive $E_{1/2}$ value of V as compared to that of the starting material I, the oxidized form of V which results in a chemical follow-up reaction (Scheme 1) is again electrolytically reduced to VI.

The main product in the preparative electrolysis is a substance with a m.p. $161°$ to $162°C$ in crude state immediately after isolation. After a chromatographic purification (in the same way as in case of oxadiazepine V) the m.p. was shifted up to $170.5°$ to $171°C$. Among the possible products this melting point is characteristical of phenazine (XII); in the literature[4] m.p. is $171 - 172°C$. The elemental analysis led to the following values: For $C_{12}H_8N_2$ (180.21) calculated: 79.98% C, 4.41% H, 15.54% N; found: 79.90% C, 4.66% H, 15.09% N. This substance gives reversible 2-electron diffusion-controlled cathodic wave over the whole pH-range; by means of the Kalousek commutator technique the corresponding reversible anodic wave is obtained. In Fig. 1 its linear $E_{1/2}$–pH plot may be observed. Dihydrophenazine results in the electrolytical reduction of phenazine the half-wave potential of which is more positive than that of the starting substance I but more negative than the half-wave potential of oxadiazepine V. The phenazine/dihydrophenazine redox system also participates in the chemical follow-up reactions during the electrolytical reduction of I.

Suggestion for an Electrochemical Reduction Mechanism of Substance I

From the mechanistic point of view, phenazine (XII) seems to be the most interesting and surprising compound among the isolated substances. In order to explain its
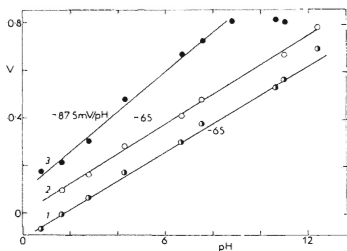

FIG. 1

$E_{1/2}$–pH Plots $(5 . 10^{-4}$ mol/l solutions). 1 oxadiazepine V; 2 phenazine XII; 3 2,2′-di-nitrodiphenyl ether I

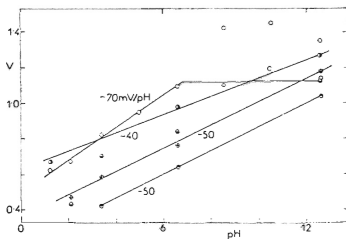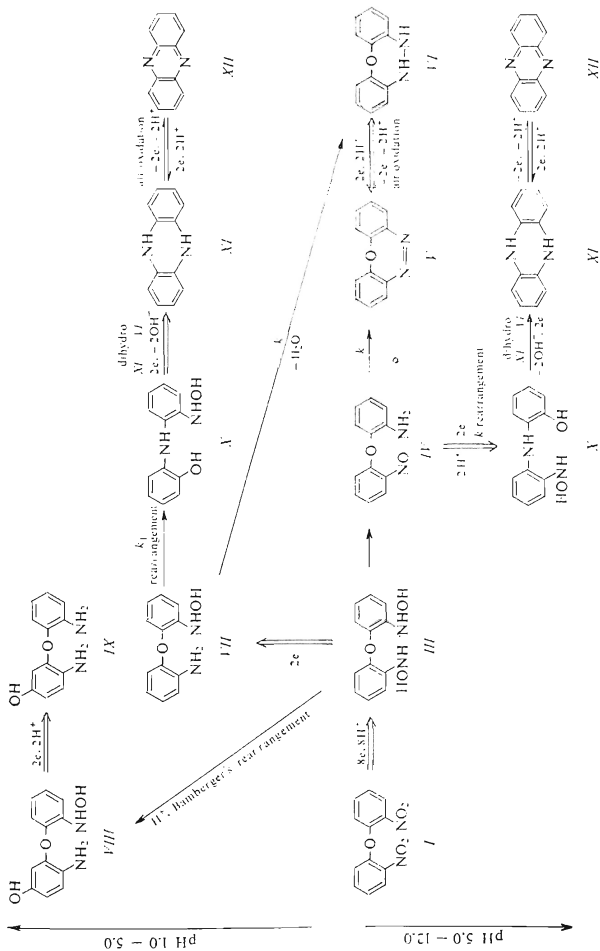FIG. 2

$E_{1/2}$–pH Plots $(5 . 10^{-4}$ mol/l solutions). ◖ Phenazine 1-oxide $XVII$, more positive cathodic wave; ◗ phenazine 1-oxide $XVII$; more negative cathodic wave; ⊕ phenazine XII, ◑ 2-nitro-2′-aminobiphenylamine; ○ 2,2′-di-nitrobiphenylamine II; ⊙ 2,2′-dinitrobi-phenylamine II, more negative wave

SCHEME 1

formation we must necessarily consider the course of all possible chemical follow-up reactions. Our explanation is based on a chemical rearrangement of the partially reduced starting nitro-compound I to a hydroxylaminohydroxydiphenylamine derivative (X) $cf.$ Scheme 1 eliminating OH^- in cyclisizing to dihydrophenazine. This conception is supported by an observation published by Roberts[10]. This authors comments on special rearrangement of 2-amino- and 2-acylaminodiphenyl ethers to 2-hydroxydiphenylamine derivatives.

In the electrolytical reduction of the starting substance I at potentials corresponding to the limiting current of the more positive cathodic wave in acid media or of the only cathodic wave in neutral and alkaline media a 4-electron reduction process occurs at each of both nitro groups (*i.e.*, in total $n = 8$) giving rise to the corresponding bishydroxylamine (III). This intermediate is somewhat stable only between pH 4·3 and 4·8.

Dibenzodiazepine (V) is formed in a sequence of reactions depicted in Scheme 1. The yield of this product is lower than that of phenazine (XII). Both V and XII with their reduced forms represent from the chemical and electrochemical point of view redox systems the oxidized forms of which electrolytically reduce at less negative potentials than the starting substance I. Consequently they evidently contribute to the course of chemical follow-up reactions of the primary bis-hydroxylamine intermediate. They assist in the reduction of the hydroxylamine group to an amino group, in particular in alkaline media where a direct electrolytical reduction of hydroxylamine is excluded. There is no doubt that an intramolecular disproportionation of the bis-hydroxylamine structure also plays a role. Basing on cp-coulometric and dc-polarographic results we ascribe the more negative wave in acid media to the further 2-electron reduction of only one of the hydroxylamine groups. The final step in the reduction of the intermediate transformed by a chemical rearrangement to a diphenylamine derivative probably occurs *via* a chemical follow-up reaction with dihydro-oxadiazepine (VI) or with the already performed dihydrophenazine (X). The oxidized-forms (XII) and (V) are regenerated by an electrochemical reduction during electrolysis of the starting dinitro compound I to reduced forms capable again of an easy chemical oxidation.

2,2'-DINITRODIPHENYLAMINE (II)

dc-Polarographic Behaviour

II is only sparingly soluble in ethanol; this is why its solutions with 75% (by vol.) ethanol in buffers and acids were studied. Fig. 2 shows the linear $E_{1/2}$–pH plot of its cathodic waves. The irreversible cathodic waves possess a diffusion controlled character and their height is a linear function of depolarizer concentration within the usual concentration range. The highest cathodic wave results in 0·5M-H_2SO_4 and

in 0·1M-HCl. At pH 3·4 it has a drawn-out character pointing to the formation of two merging waves. The voltammetric curve recorded in this media with a stationary hanging mercury-drop electrode exhibits two well-separated cathodic peaks with $E_{p/2}$ −0·69 and −0·88 V ($E_{1/2}$ of the single reduction wave at the dme is −0·94 V *vs* M.S.E.). Similar well-separated cathodic peaks can be observed at all other pH values investigated here if a hanging mercury drop is used. The ratio of heights of polarographic waves is 3 : 2 in the range from pH 0·3 to 7·5. Above the later value the ratio changes to 3 : 1. The cathodic waves are more clearly separated on *i–E* curves obtained in weakly acidic and weakly alkaline media. At pH > 10 their separtion is so clear that their $E_{1/2}$ values can be measured. Their total height, however, is lower than that in the acid region. In a 0·2M-NaOH solution the dc-polarographic wave exhibits two well-separated reduction waves whose heights are in the ratio 1 : 1. Anodic waves on a commutated *i–E* curve recorded with the Kalou-

TABLE III

Products and cp-coulometric results from $5 . 10^{-4}$M 2,2′-dinitrodiphenylamine (*II*) in media with 75% (by vol.) ethanol. A at the potential adjusted to the limiting current of the more positive wave; B at the potential adjusted to the limiting current of the more negative wave

pH	Solution	TLC analysis of the mixture products after electrolysis	Number of electrons	
			A	B
1·25	0·5M-H₂SO₄	nitroamine (*XIII*) phenazine N-oxide (*XVII*)	11·0	—
2·1	0·1M-HCl	phenazine (*XII*) phenazine N-oxide (*XVII*) nitroamine (*XIII*)	9·7	
3·4		nitroamine (*XIII*) A phenazine (*XII*) both A and B phenazine N-oxide (*XVII*) both A and B	8·5	10·3
6·6			5·8	11·6
8·55		nitroamine (*XIII*) A phenazine (*XII*) both A and B phenazine N-oxide (*XVII*) both A and B	7·5	10·0
10·5			11·6	
12·6		phenazine (*XII*) both A and B phenazine N-oxide (*XVII*) both A and B	7·25	10·5

sek commutator, which correspond to the oxidation of the hydroxylamine group formed in the reduction of the nitro group during the generation period, were obtained with substance *II* only in 0·5M-H_2SO_4 and then at pH > 6·0.

cp-Coulometric Measurements

The results of microcoulometric measurements performed with substance *II* are summarized in Table III. The qualitative composition of the reaction mixtures is also shown in the same Table III. During microelectrolysis in strongly acidic media the colour of the catholyte turns green or even, later, blue; no oxidation wave results, however. At pH 3·4 — but also in neutral and alkaline solutions — the catholyte turns yellowish green during microelectrolysis and a small oxidation wave forms. Towards the end of microelectrolysis the catholyte becomes colourless again. If the microelectrolysis takes place in 0·2M-NaOH (pH 12·6) and with the reduction potential adjusted to a value corresponding to the limitting current of the more positive wave the catholyte turns orange and an anodic wave and a new more negative cathodic wave appear. If in this solution the electrolysis takes place at the potential of the more negative cathodic wave, no anodic wave forms.

cp-Preparative Electrolysis

Because of low solubility, the normally applied concentration in preparative electro-lysis of substance II, *i.e.* 2·5 . 10^{-3} mol l^{-1}, was only used in non-aqueous media (*e.g.* ethanol with 0·5M-LiCl or acetonitrile with 0·1M-N(n-C_4H_9)$_6$PF$_4$, total volume 0·3 l). A polarogram recorded at the beginning of an electrolysis in 0·5M-LiCl in ethanol showed two well-separated cathodic waves. The potential was then adjusted to a value corresponding to the region between the two waves. The starting current was 800 mA. The colour of the solution changed from orange to yellow and a charge of 1 400 C ($n \doteq 14.5$) was consumed. But a small anodic wave was observed on the control polarogram. Ethanol was removed from the catholyte in a vacuum evaporator and the solid residue was suspended in about 80 ml of distilled water. The solution thus formed was then extracted with chloroform. After evaporating in a vacuum evaporator the solvent from the dried extract (anhydrous CaCl$_2$) 189 mg of a mixture of products was obtained. Thin layer chromatography making use of standard compounds revealed that this mixture contains phenazine (*XII*), phenazine N-oxide. (*XVII*) and the nitroamine (*XIII*). When electrolysing in buffered media containing 25% (by vol.) water it was necessary to decrease the concentration of *II* to 1·25 . 10^{-3} mol/l in order to keep it in the solution. Even so, the electrolysis proceeded with a non-equivalent much higher electron consumption and an interaction with the working mercury cathode occurred, accompanied by evolution of tiny gas bubbles even if no current was passing. Most probably it is nitrogen. We were unable to prove formation of ammonia with the Nessler reagent. This phenomenon can be only

observed with intense preparative electrolysis at higher concentrations of *II*, not in microelectrolysis or in polarography. The product of these large-scale electrolyses was again phenazine (*XII*), nitroamine (*XIII*) and phenazine N-oxide (*XVII*). The main product of the electrolysis in 0·1M-HCl was 2,2'-diaminodiphenylamine (*XVI*).

Isolated Products and their Polarographic Behaviour

2,2'-Diaminodiphenylamine (XVI). By chromatography of the mixture of products after electrolysis of *II* in 0·1M-HCl (25% by vol. C₂H₅OH) on a column (silica gel L 100/150 Lachema) in the system benzene–ether a substance was isolated which in crude state melted at 85−86°C. It is polarographically inactive. The crystallized product melting at 99·5−100°C yielded the following data in elemental analysis: For $C_{12}H_{13}N_3$ (199·25) calculated: 72·33% C, 6·57% H, 21·18% N; found: 71·91% C, 6·81% H, 21·15% N.

The ms pointed to the formation of the molecular ion M^+ 199 *m/e* and further fragments 184 *m/e*, 182 *m/e*, 181 *m/e*, 91 *m/e*. These data are in agreement with the structure of diamine *XVI*.

Phenazine N-oxide. After a chromatographic separation (column with silica gel L Lachema; benzene, 2·5% acetic acid) a yellow substance was obtained which exhibited a m.p. of 222·0−222·5 °C (sealed capilary) combined with a strong sublimation (according to literature m.p. 223°C). From its mass spectra the existence of the following fragments was deduced: 196 *m/e*, 180 *m/e*, 179 *m/e*, 170 *m/e*, 168 *m/e*. As regards its dc-polarographic activity two cathodic waves of equal height were observed over a broad range of pH-values. These waves are diffusion-controlled and their heights are a linear function of concentration. cp-Coulometric measurements proved each wave corresponds to an uptake of two electrons. The $E_{1/2}$–pH plots of the waves are shown in Fig. 2. Making use of the Kalousek commutator (rectangular discontinuous voltage) it has been observed that a commutated anodic wave only appears with only the potential E_{aux} in the generation phase corresponding to the potential of the limiting current of the more negative cathodic wave. The $E_{1/2}$-values of this anodic wave correspond to $E_{1/2}$ of phenazine (*XII*). In the less negative cathodic wave a 2-electron reduction of the N-oxide to phenazine occurs whose reversible reduction takes place at the potentials of the second wave. It follows from the above properties of the isolated compound with m.p. 222−222·5°C that it is actually phenazine N-oxide (*XVII*).

After isolation from the mixture of products of the preparative electrolysis phenazine (*XII*) was identified by TLC analysis making use of a standard isolated already after the electrolysis of *I*. For the sake of comparison the $E_{1/2}$–pH plot of its cathodic wave under identical conditions (as those for the three other compounds) is shown in Fig. 2.

2-Nitro-2′-aminodiphenylamine (XIII) has been prepared as a model standard. Its polarograms showed a single, irreversible, cathodic, diffusion-controlled wave. Only in the neutral region a second cathodic wave resulted. The $E_{1/2}$–pH plot of these cathodic waves may be also inspected in Fig. 2. cp-Coulometric measurements revealed that in the neutral region at pH 6·6 each of the two cathodic waves corresponded to a 4-electron process; at pH 3·4, however, the total consumption is about 5 electrons per molecule. The measurements with the Kalousek commutator never yielded an anodic wave both in acid and alkaline solutions. In neutral media commutated anodic waves were observed differing according to the potential E_{aux} in the generating cycle phase. Phenazine (XII) has been isolated by TLC as the main product of the microelectrolysis of the nitroamine XIII. The other products were only minor impurities.

Discussion of Results with Substance II

The electrolytical reduction of aromatic nitro group in the compound II takes place in an unusual way. It follows from the above results that the structure of this symmetrical dinitro compound enables a partial reduction of only one nitro group; moreover, this reduction proceeds in a single dc-polarographic wave. The following interpretation can be offered: in 2,2′-dinitrodiphenylamine II the protonation of the nitrogen atom in the amino group separating both phenyl groups inhibits a transfer of both mesomeric and inductive effects since hyperconjugation is excluded. This forms a basis of the non-equivalence of both symmetrically substituted benzene nuclei. On one of the nitro groups an electron transfer occurs which causes such a distribution of the electron density over the substrate molecule that the 6-electron process takes place at the electrode only in the one nitro group originally involved (Scheme 2). The 6-electron reduction of an aromatic nitro group in a single step is made possible by the structure of *o*-phenylaminonitrobenzene and also takes place with *o*-nitrothiophenol or with 2,6-dinitroaniline[11]. The course of a one step 6-electron reduction is probably enabled by the mesomeric *o*-quinoid structure of the 2-hydroxylamino-2′-nitrodiphenylamine intermediate which easily releases the hydroxyl anion from the hydroxylamine group. The nitroamine XIII which represents the product of an electrode process taking place at potentials corresponding to the more positive cathodic wave further reduces with the consumption of 4-electrons within the whole pH-range, giving rise to 2-amino-2′-hydroxylaminodiphenylamine (XIV). Since we never succeeded in finding in the mixture of products the well-known (but only with difficulty accessible) heterocyclic product — dibenzo-(*b*, *e*)-(1,4,5)-triazepine (XV), one can assume that the intramolecular chemical interaction between NH$_2$ and NO (this being a condition of its formation) does not occur because of instability of the intermediate XIV. In a similar manner the formation of 2,2′-diaminodiphenylamine (XVI) is limited — exceptionally — only to strongly acidic media. Over a broad
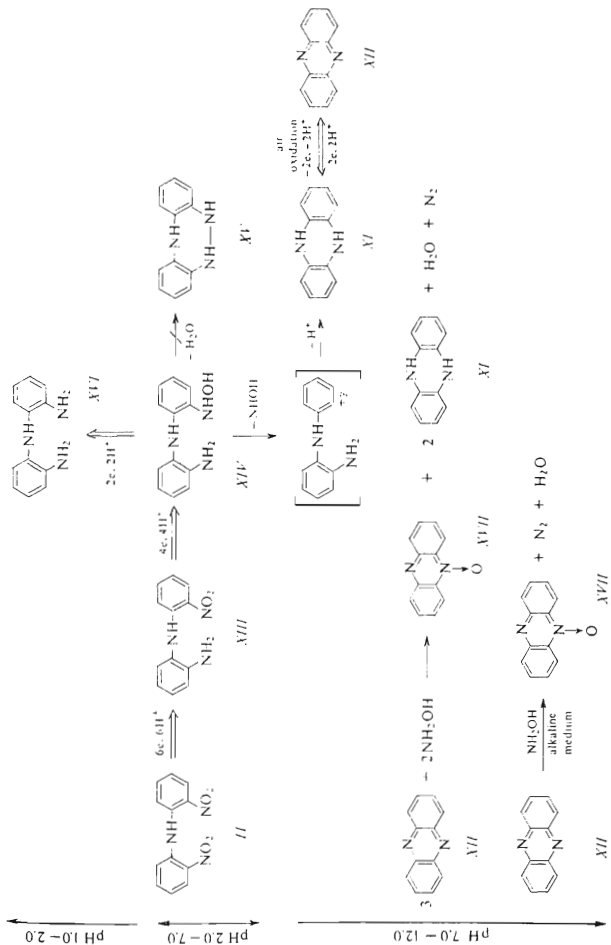
SCHEME 2

region of pH-values however, phenazine (*XII*) or its N-oxide (*XVII*) results. On the other hand, the formation of these two substances requires the loss of a nitrogen atom from the molecule of the starting substance *II*. We assume that it proceeds by an elimination of a hydroxylamine group of the intermediate *XIV* with the whole electron pair (Scheme 2). The hydroxylamine anion set free reacts with a proton giving rise to hydroxylamine which reacts chemically with phenazine *XII*. Phenazine N-oxide (*XVII*) is formed and hydroxylamine reduces to water and nitrogen. We assume that the oxidant proper attacking phenazine (*XII*) is N_2O; this is set free either in the reaction of NH_2OH with phenazine or in an alkaline decomposition of NH_2OH (the alkaline solution in the vicinity of the mercury cathode during electrolysis or alkaline solutions in general). Dihydrophenazine (*XI*) easily undergoes a chemical oxidation to phenazine (*XII*) which, in turn is electrolytically reduced to the reduced form *XI* at a more positive potential than the starting substance *II*. Its electrochemical reversibility enables phenazine to participate in follow-up chemical reactions taking place after the electrode process proper. It has been proved that no ammonia is set free during electrolysis.

CONCLUSIONS

On comparing the half-wave potentials of both substances studied in this paper it has been observed that 2,2'-dinitrodiphenyl ether (*I*) reduces more easily. However, considering the formation of two poorly separated dc-polarographic waves both in acid and neutral solutions and the fact that only an average $E_{1/2}$ of this double wave is measured, this statement is not quite plausible.

The dinitro compound *I* undergoes an electrolytical reduction in an eight-electron wave to the corresponding bis-hydroxylamine; this occurs over the whole pH-region. This bis-hydroxylamine intermediate exhibits a reactivity enabling an intramolecular disproportionation which is linked with a further chemical follow-up cyclization reaction giving rise to a dibenzooxadiazepine. As a competing chemical reaction which desactivates the product of the above disproportionation a special chemical rearrangement (*cf.* literature data[10]) in which the starting diphenyl ether structure is transformed to a diphenylamine.

The resulting intermediate undergoes a chemical follow-up cyclization reaction and yields dihydrophenazine. This substance which is the main product over the whole pH-range studied here, results also in the acid region owing to a 2-electron reduction of the 2,2'-bishydroxylamine derivative; this reaction takes place in the second, more negative wave. The intermediate formed here in the electrode reaction is again subject to a chemical rearrangement to a hydroxydiphenylamine structure and finally results in the formation of dihydrophenazine. A part of the bishydroxylamine primary intermediate is inactivated in strongly acidic media in a Bamberger rearrangement followed by a 2-electron uptake at more negative potentials.

Completely different is the electrolytical reduction of the dinitro compound *II*. Its structure makes possible a mesomeric transition to an *o*-quinoid form and, consequently, an easier reduction of the hydroxylamine group to amine. Moreover, the circumstance, that the nitrogen atom in the connecting link of the whole system affects (according to the pH-value of the solution) the degree of conjugation and of the transfer of inductive effects, supports the electrolytical reduction of a single nitro group in *II* to an amino group. The primary product after electrolysis at positive potentials is 2-amino-2'-nitrodiphenylamine. At more negative potentials a 4-electron reduction of the other nitro group takes place resulting in a mixed 2-amino-2'-hydroxylamino derivative.

Dibenzotriazepine is not formed in the electrolytical reduction on mercury electrodes; this may be due to the anomalous behaviour of this compound the reduced form of which has not been prepared as yet.

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Translated by the author (J. V.).