ELECTROLYTIC REDUCTION OF *o*-NITROBENZYL THIOCYANATE IN BUFFERED SOLUTIONS ON MERCURY

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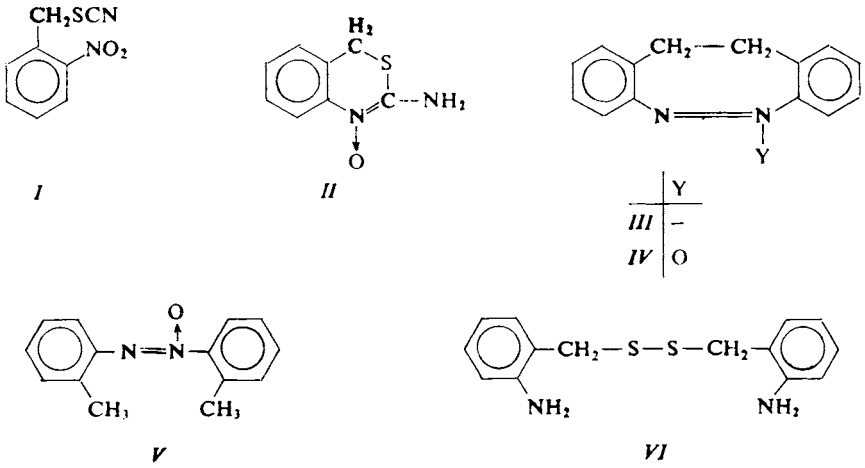
The *o*-nitrobenzyl thiocyanate (*I*) behaves differently on the DME and on a large mercury pool electrode. Polarography did not give a sufficiently clear explanation of the reaction mechanism, only the preparative experiments yielded useful results. Whereas polarographic curves in solutions of Britton–Robinson buffer system with 50% by vol. ethanol exhibit two cathodic waves within the pH region 1—12, corresponding according to their height ratio to an uptake of 4 e and 2 e respectively, the controlled potential preparation electrolysis (CPE) and coulometry results indicate a more complicated reaction path. In the CPE carried out at the concentration of *I* $1 \cdot 10^{-2}$ mol/l the electroreductive splitting of CH_2—SCN occurs as the first step. Nitrobenzyl radicals so formed react in the follow-up dimerization resulting in dibenzyl or toluene structures. Simultaneously or at a later stage the completion of the electrolytic reduction of the nitro group proceeds to the hydroxylamino group. In solution of $9 > pH > 1$ the CPE of nitro compound *I* takes place by an ECEC mechanism yielding dibenzodiazocine *III*, its N-oxide *IV* and 2,2′-dimethylazoxybenzene (*V*). In course of preparative electrolysis in strongly acidic medium 2-aminobenzo(1,3)-thiazine-1-oxide (*II*) is formed by an EC mechanism.

The mutual interaction of NO_2 and SCN groups bound on the aromatic nucleus in electrolytic reduction on a mercury cathode was first investigated in the system of *o*-nitrobenzene thiocyanate[1]. The stability of the thiocyano group strongly depended, apart of the pH of the solution, also on the stage of the electrolytic conversion of the vicinal nitro group.

In order to know more about the change of the mutual effect between the thiocyano and nitro group in the electrolytic reduction when one of the groups is separated from the benzene ring by some other atom we chose *o*-nitrobenzyl thiocyanate (*I*) for our investigation. We wanted to see whether a follow-up chemical intramolecular cyclization occurs and how the separated thiocyanate group behaves.

Bartak and coworkers[2] studied the electrolytic reduction of *p*-nitrobenzyl thiocyanate in acetonitrile solution of 0·1M-Et_4NClO_4. By means of cyclic voltammetry they found that the uptake of one electron takes place under the formation of a radical anion with a following elimination of the thiocyano group. By controlled potential preparative electrolysis in the same solution they obtained *p*-nitrotoluene and 4,4′-dinitrodibenzyl as products.

The nitro compound *I* has not yet been electrochemically studied. First its dc-polarographic behaviour was followed and then it was subjected to controlled-potential electrolysis with a large-area Hg electrode; the results of these investigations are the subject of the present communication.



SCHEME 1

EXPERIMENTAL

The polarograph LP 9 in connection with the XY recorder 4103 used for the polarographic studies are produced by Laboratorní přístroje, Prague. In all cases the saturated mercury sulphate electrode (M.S.E.) served as reference electrode. All polarographic records were made in the three electrode mode.

The preparative electrolysis proceeded at controlled potential making use of the performance potentiostat Betatest P 80 10 constructed and produced by the Laboratory of Power Sources in Sophia (Bulgaria); a preparative cell described in the preceding report[1] was used. An aqueous solution of sodium sulphate or of 0·1M-H_2SO_4 served as anolyte, a graphite block or a stainless steel gauze was used as anode. 2-Nitrobenzyl thiocyanate was prepared from 2-nitrobenzyl chloride by a described procedure[3]. The solutions used for the investigation of the electrochemical behaviour of compound *I* contained always 50% by vol. of ethanol. The TLC analyses were carried out on the Silufol UV 254 sheets made by Kavalier, Czechoslovakia. Silica gel L (110—115 μm) of the same company was used for the separation by the column chromatography in the solvent system benzene/50% by vol. dichloromethane. The mass spectra were recorded by means of the Jeol MS 100 mass spectrometer.

Controlled potential preparation electrolysis (CPE) *of nitrocompound* I *in strongly acidic solution*: The solution of *I* ($1 \cdot 10^{-2}$ mol/l (388 mg) in 0·1M-HCl with 50% by vol. ethanol) was electrolysed at the potential in the range of the limiting current of the more positive cathodic wave (—0·8 V *vs* S.M.E.). The polarographic curves of the clear colourless catholyte recorded during the electrolyses showed a decrease of both cathodic waves and the formation of a new distorted anodic wave. After passing the charge of 1 465 C (7·6 F/mol) when the current amounted to as much as 10 mA the electrolysis was stopped. The catholyte was neutralized by an aqueous NaOH solution and thereafter extracted by $CHCl_3$. When the solvent was removed a brownish-yellow greasy substance remained. Its TLC analysis indicated that it contained N-oxide *II*, dibenzodiazocine N-oxide *IV* and azoxytoluene *V*. The next extraction of the water layer of the catholyte yielded 120 mg of a yellowish substance melting at 167·5—168·5°C (after recrystallization from ethanol) which was identified as 2-aminobenzo(1,3)-thiazine N-oxide. A similar electrolysis

performed at a potential corresponding to the limiting current of the more negative cathodic wave was followed under the consumption of 10·8 F/mol by formation of an insoluble mercury compound.

CPE *of* I *in a weakly alkaline region at* pH 8·3: When the potential was set at the value corresponding to the limiting current of the more positive cathodic wave (−1·6 V *vs* S.M.E.) both cathodic waves diminished and a new anodic one appeared. After the passage of 6 F colourless catholyte was treated as before. The yellow greasy substance represented a mixture of azoxytoluene *V* and N-oxide *IV*. They were separated by means of a silica gel chromatographic column. Carrying out an analogous electrolysis (pH 8·3) at the potential of the more negative cathodic wave 7 F was consumed and the polarographic record exhibited two anodic waves. After treatment of the catholyte we obtained a product mixture, containing in addition to *V* and *IV* a yield of 42% of dibenzodiazocine *III*.

2-Aminobenzo(1,3)-thiazine N-oxide (*II*) was isolated after electrolysis in the strongly acidic medium. The yellowish substance melting at 167·5—168·5°C is soluble in ethanol. The m.s. analysis provided M^+ 180 *m/z* and the fragments 164, 121 *m/z etc.* The substance is polarographically inactive and only in neutral solution gives the cathodic wave of catalytic hydrogen evolution. Both the described behaviour of the analogous substance and our observation show that this benzo(1,3)thiazine derivative *II* has a strong tendency to associate.

5,6-Dihydro-dibenzo(*c*,*g*)-(1,2)-diazocine (*III*) resulted in the product mixture obtained by CPE in neutral and alkaline solutions (at potentials corresponding to the more negative wave). The pure substance was obtained by column chromatography on silica gel. It was then further purified by sublimation *in vacuo* (200—300 Pa) at 80—90°C. The yellow crystalline substance melted at 110—111°C (literature[4,5] gives for the diazocine *III* structure a m.p. 112—113°C or 111°C). The m.s. record of that substance yielded M^+ 208 *m/z* and the fragments 207, 180, 179, 178 *m/z*. Its polarographic investigation gave two irreversible cathodic waves increasing linearly with concentration and fulfilling the linear $E_{1/2}$-pH dependence (Fig. 3). The commutated polarographic curve only gave an irreversible anodic wave in strongly alkaline solution at pH $\geqq$ 11. In strongly acidic media an additional, small, more negative cathodic wave appears.

5,6-Dihydro-dibenzo(*c*,*g*)-(1,2)-diazocine N-oxide (*IV*) was obtained from the product mixture of the CPE in weakly acidic to weakly alkaline solution. By column chromatography a fraction was obtained, which contained a yellowish crystalline substance melting at 158·5—160·5°C (for dihydrodibenzodiazocine *IV* literature[4] presents a m.p. of 154°C). The record of the mass spectrum exhibited the M^+ 224 *m/z* and the fragments 223, 207, 206, 178 *m/z etc.* This substance is polarographically reduced in a 4 electron cathodic wave within the pH region of 1—12 and in the pH region 1—8 it fulfills a linear $E_{1/2}$ *vs* pH dependence (Fig. 3). In strongly alkaline media an anodic commutated wave was obtained the $E_{1/2}$ of which corresponds to that obtained during the diazocine *III* study under identical conditions.

The 2,2′-dimethylazoxybenzene (*V*) was chromatographically separated from the reaction mixture after the CPE in weakly acidic to alkaline media firstly as a yellow oil which later solidified to a yellow crystallinic mass melting at 45·5—46·5°C (literature[6] describes two diastereoisomers melting at 59°C and 82°C, respectively). The ms. analysis recorded the M^+ 226·1 *m/z* and the fragments 225·1, 211·0 and 209·1 *m/z*. In strongly acidic medium (pH $\leqq$ 2·5) this substance gave two cathodic waves corresponding to the uptake of 4 e and 2 e, respectively. They demonstrate the reduction to a hydrazoderivative and finally to the *o*-toluidine. When the auxiliary potential was set in the limiting current region of the more positive cathodic wave a commutated anodic wave was recorded, while when applying a more negative auxiliary potential the anodic wave did not appear. One 4 e cathodic wave shows in the range of pH $>$ 2·5. At pH $>$ 5 the isolated substance gives two kinetic cathodic waves. The sum of their heights is constant and equivalent

to the height of the 4 e wave. The more positive cathodic wave corresponding to the reduction of protonated species of the azoxy derivative diminishes with increase of pH, while the height of the more negative cathodic wave increases. The cathodic wave of the 4 e reduction of the azoxy-compound *V* provides a linear $E_{1/2}$ *vs* pH dependence over the whole pH region (Fig. 3). The more negative cathodic wave gives also this linear dependence but in the range of pH > 5·5.

RESULTS AND DISCUSSION

Polarography

The solution of $5 . 10^{-4}$ mol/l nitro compound *I* gives two cathodic waves in the whole pH range (Britton–Robinson buffers with 50% by vol. ethanol), which are in the mutual height ratio 2 : 1. These waves are diffusion-controlled, showing a linear concentration dependence up to $c = 2{\cdot}5 . 10^{-3}$ mol/l. The more positive wave gives a linear $E_{1/2}$ *vs* pH dependence in the region studied and is most likely due to the four electron reduction of the nitro group to the hydroxylamino group (Fig. 1). The Kalousek switch yields an anodic wave corresponding to the oxidation of hydroxylamine to the nitroso derivative. The same result is obtained with a cyclic voltammogram on the HMDE where a small cathodic peak of the NO reduction to NHOH may be also observed, in particular at pH ≧ 5·0.

The more negative cathodic wave yields a linear dependence of $E_{1/2}$ *vs* pH in the acid region for pH ≦ 5. No anodic wave on the commutated curve was recorded under these pH conditions by means of the Kalousek switch when an auxiliary potential corresponding to more negative cathodic wave was applied. It is also probable, that this two-electron cathodic wave corresponds under these conditions to the hydroxylamino group reduction to the amino group. At pH > 5·5 the $E_{1/2}$ of the more negative cathodic wave is pH independent (Fig. 1). According to our experience with this type of substrates[1], it points to a 2e-reductive splitting of CH_2S— CN. When the curve with the Kalousek switch is recorded under these conditions (at pH > 5·5

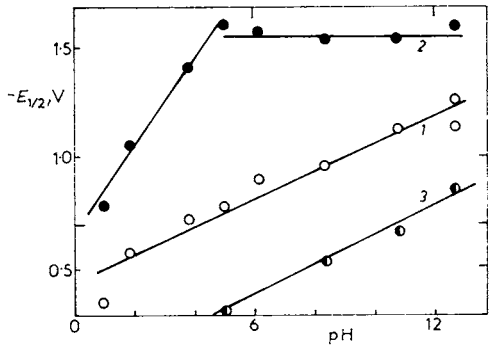


FIG. 1

$E_{1/2}$-pH plot for $5 . 10^{-4}$ mol/l-nitrobenzyl thiocyanate in Britton–Robinson buffers with 50% by vol. ethanol. *1* more positive cathodic wave; *2* more negative cathodic wave; *3* commutated anodic wave (E_{aux} at the limiting current of the more positive cathodic wave)

and at the auxiliary potential corresponding to the limiting current of the more negative cathodic wave) an anodic wave appears. It can correspond both to the hydroxylamine oxidation to the nitroso derivative and to the oxidation of *o*-aminobenzylthiol (formed by the mentioned 2 e reduction occuring in the more negative cathodic wave) to the corresponding disulfide or a compound with Hg. We assume, that the $E_{1/2}$ for the both oxidations are so close that the equivalent anodic waves are fused[1]. Unfortunately no distinctly separated anodic wave on the switched curve was found for CN^- ions splitted off at potentials of the more negative cathodic wave (during the —SCN reduction). The voltammetric curves recorded with a HMDE show in the pH region 1·5–6·5 only a single distinct cathodic wave with a long limiting current plateau, pointing to the existence of further suppressed more negative cathodic wave. However, in an ideal case, *e.g.* in acid solutions, three cathodic waves should develop for substance *I* in DC polarography: two cathodic waves for aromatic nitro group reduction and a more cathodic one for the SCN group reduction. We found this case with *o*-nitrobenzene thiocyanate where the second and third more negative cathodic waves were only undistinctly separated. In case of *I* the electrochemical reaction mechanism seems to be more complicated and both more negative waves coalesce if they are present.

As to the appearance of anodic waves on switched curves at pH > 5 when applying auxiliary potential of both cathodic waves, they exhibit only irrelevant $E_{1/2}$ shift each other and their height difference is negligible. Since aromatic hydroxylamines are at pH > 5 usually irreducible[1] we can ascribe the more negative cathodic wave to the reductive cleavage of the —SCN group.

In the strongly alkaline region with pH ≧ 9·5 a cathodic prewave is distinctly visible; it is better observable on the voltammetric curve recorded with a HMDE also in weakly alkaline solutions. When the concentration of nitro compound *I* increases over $2{\cdot}5 \cdot 10^{-3}$ mol/l the shape of the polarographic curves changes (Fig. 2*a*, *b*). Three cathodic waves appear in the weakly acidic, neutral and weakly alkaline solutions, the two more positive of which are not perfectly separated. When the ethanolic stock solution of the nitro compound *I* is added to the strongly alkaline solution (pH > 10) a distinct small anodic prewave appears and the solution turns pale yellow. The solvolytic equilibrium cleavage occurs in the SCN group giving rise to the benzylthiolate anion as expected[1].

CP-*Coulometry*

Coulometric determinations performed at the large area mercury electrode in the microcell (surface area approx. 1 cm^2) gave the following results ($5 \cdot 10^{-4}$ mol/l of nitro compound *I*, buffered solution with 50% by vol. ethanol with potential set at a value corresponding to the limiting current of the first more positive cathodic

wave):

pH	0·6	5·2	9·2
n/e	5·1	5·0	4·9

The coulometric determination in the solution of pH 9·2 at the potential of the limiting current of the most positive cathodic prewave gave n value as high as 1·4 e (with polarographic concentration of *I*). When coulometry was performed in the solution $1 \cdot 10^{-2}$ mol/l of *I* at pH 6·6, the n value amounted to 4·8 e.

The exact coulometric measurements also demonstrated that in the first cathodic wave an electrolytic reduction takes place, which consumes about one electron more than it is necessary for the assumed reduction of the aromatic nitro group to the hydroxylamino derivative.

Controlled Potential Preparative Electrolysis

From the results of the preparative electrolysis in weakly acidic, alkaline and neutral media it follows that there occurs the elimination of the whole SCN group. The presence of thiocyano anions was proved in catholytes after the CPE by the simple test with Fe^{3+} ions which was also carried out with the catholyte before the electrolysis. The distorted most positive anodic wave appearing on polarographic curves during the CPE was ascribed, on the basis of the standard addition method, to the anodic reaction of the eliminated SCN anions with Hg ions.

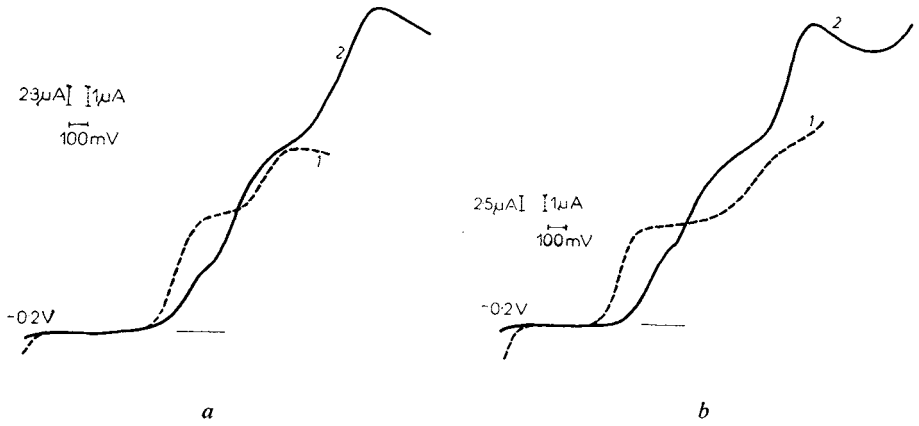
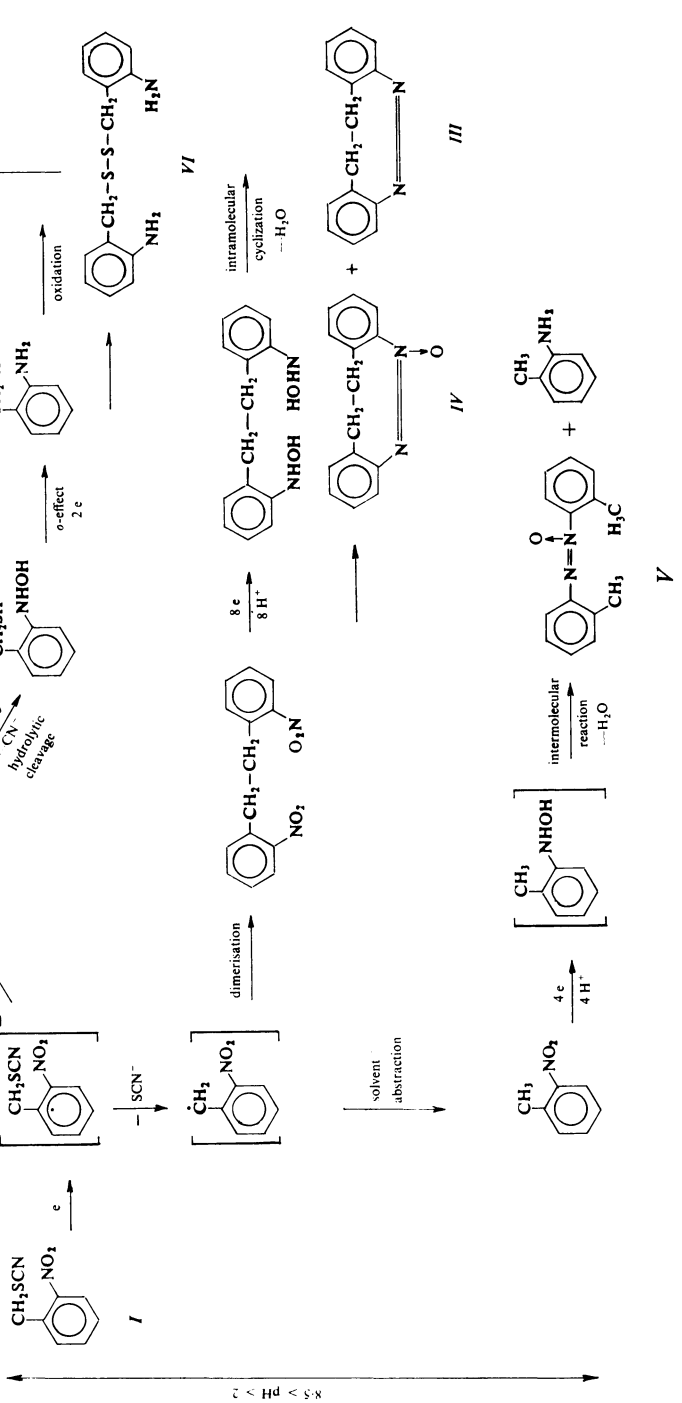


FIG. 2

a Polarographic curves of *o*-nitrobenzyl thiocyanate in Britton–Robinson buffer solutions with 50% by vol. ethanol, pH 5·0. *1* $5 \cdot 10^{-4}$ mol/l; *2* $2{\cdot}5 \cdot 10^{-3}$ mol/l; *b* The same conditions as in Fig. 2*a*, pH 8·3


strongly acidic
solutions pH < 1.5
strongly alkaline solutions pH > 9
pH > 9
CN⁻ hydrolytic cleavage
intramolecular cyclization k
o-effect
2 e
oxidation
dimerisation
8 e
8 H⁺
intramolecular cyclization
−H₂O
solvent abstraction
intermolecular reaction
−H₂O
4 e
4 H⁺
−SCN⁻
e
I
II
III
IV
V
VI

SCHEME 2

The experiments carried out so far outline (especially when performed at potentials of the most positive cathodic wave) that the elimination of the SCN group takes place simultaneously with or before the electrolytic reduction proper of the nitro group. With respect to the isolated products we finally come to the opinion that the SCN elimination occurs as the step next to the radical anion formation after the uptake of 1 electron (Scheme 2). Also despite water–ethanolic solutions the reductive elimination of the SCN group followed by radical dimerization, described by Bartak and coworkers[2] for aprotic solutions, proceeds primarily. The polarographic records of catholytes after the CPE exhibit two anodic and one low cathodic wave. The more positive anodic wave ascribed to the anodic reaction of eliminated SCN anions, is distorted and partly overlaps with the more negative anodic wave. With respect to the product mixture composition these anodic waves are significant. All isolated electroactive products are reduced namely more positively than the starting substance *I* (Fig. 1, 3) and can partly form during catholyte processing and products isolation on air. The remaining low more negative cathodic wave occurring on DC records after the CPE demonstrates the formed azoxy derivatives (*IV* and *V*).

A clearer and simpler reaction EC mechanism explains the formation of benzo(1,3)-thiazine *II* in strongly acidic solution (Scheme 2). In a strongly alkaline solution the visible hydrolytic cleavage CH_2S—CN takes place in course of the CPE consuming 4·3 e. The TLC analysis of the product mixture yielded 2,2′-diaminodibenzyldisulfide (*VI*) as the main product. Its formation proceeds despite the alkaline solution (where NHOH is usually irreducible) owing to an *o*-effect resembling *e.g.* that in *o*-hydroxylaminothiophenol[1].

We can conclude, that the results of electrochemical studies of the nitro compound *I* on the DME differ from those obtained on a large mercury pool electrode in the CPE. The polarographic records of substance *I* give undistinctly developed more negative cathodic waves due to the near $E_{1/2}$ values of the cathodic processes. The results of the DC polarography recorded in solutions of *I* at $c \geqq 1 \cdot 10^{-2}$ mol/l seem to illustrate the behaviour during the CPE.

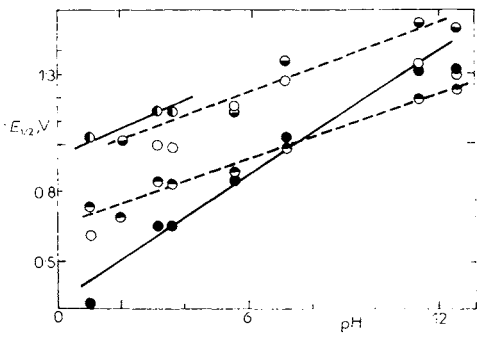


FIG. 3

Plot of $E_{1/2}$-pH for $5 \cdot 10^{-4}$ mol/l products from the CPE in Britton–Robinson buffer–ethanolic solutions. Dibenzodiazocine N-oxide *IV*: ● more positive cathodic wave, ◐ more negative cathodic wave; full lines; dibenzodiazocine *III*: ○ cathodic wave; azoxytoluene *V*: ◓ more positive cathodic wave; ◒ more negative cathodic wave; dashed lines

The coulometry and CPE outline the course of chemical follow-up reactions (Scheme 2). After the first electron uptake the radical anion of the nitro compound *I* is created which eliminates the thiocyano group giving rise to the nitrobenzylic radical. These neutral radicals either dimerize with a dihydrostilbene structure formation or they are transformed into the toluene derivatives.

The dibenzodiazocines *III*, *IV* and azoxytoluol *V* were mainly found in the product mixture from the CPE performed in the pH region between 9 and 2. They are formed by a ECEC mechanism. The benzo(1.3)thiazine *II* is created through the following intramolecular cyclization (the EC mechanism) from the starting nitro compound *I* in a significant yield (75%) in strongly acidic solution. Owing to its difficult isolation because of the strong association tendencies no precise quantitative experiments were made.

The obtained dibenzodiazocine derivatives *III* and *IV* behave, when studied polarographically, like the intramolecular azoxy and azo compounds with excluded conjugation in the heterocyclic ring. The electrochemical redox reversibility of the hydrazo- and azo-structures significant of the dibenzo(1,2)diazepine derivatives[7] (*e.g.* the dibenzo(*b*,*f*)-(1,2-)diazepine N-oxide) appears in dibenzo(1,2)diazocines *III*, *IV* only to a small extent in strongly alkaline media. This behaviour of dibenzodiazocines is likely due to the insertion of a further methylene group between the two benzene nuclei connected by the azo group and resulting in the formation of a eight-membered heterocyclic ring. This causes a twisting of the planes of both π-systems this being unfavourable for long-distance conjugation, in particular in the reduced species.

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