

## FORMATION OF BENZOTHAZOLE DERIVATIVES IN THE ELECTROCHEMICAL REDUCTION OF *o*-NITROTHIOCYANOBENZENE

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*o*-Nitrothiocyanobenzene was used as a model substance in investigating the effects of different factors on the electrochemically initiated intramolecular reaction and the possibilities of its application in organic synthesis. The results of a detailed polarographic study of this substance over a wide area of pH values in buffered solutions containing water and ethanol as solvents are compared with results of coulometric measurements and preparative electrolyses at different potentials of a large-area mercury electrode. Basing on these results a system of electrode and chemical follow-up reactions has been suggested which can lead to the formation of 2-amino-benzothiazole 3-oxide, 2-aminobenzothiazole or *o*-aminothiophenol.

The preparative electrolysis of organic substances will be less probably based on the electroreduction or electrooxidation of a single functional group or grouping, than on a sequence of chemical follow-up reactions initiated by an electrode reaction. Such a reaction can be exemplified by the so-called electrochemical cyclization reactions; here, the framework of the starting substance is substituted by groups in sterically favourable orientation, at least one of them being electroactive. The actually reacting group results in the electrode reaction, and undergoes a chemical interaction with the neighbouring group attached to the same molecule giving rise to a new structural arrangement. *o*-Nitrothiocyanobenzene *I* has been chosen as a model substance for studying the course and the possibilities of a synthetic application of such a reaction. The polarographic investigation was first performed by Bellavita and coworkers<sup>1</sup>. A preparative electrolytical reduction of this substrate was made by Fichter and Beck<sup>2</sup>. In a constant-current electrolysis at a lead cathode in 2N-H<sub>2</sub>SO<sub>4</sub> these authors obtained 2-aminobenzothiazole *II*, at a copper cathode 2-amino-5-hydroxythiocyanobenzene under otherwise identical conditions. More recent electrochemical investigations of *I* were carried out by Lund and Feoktistov<sup>3</sup>. Here 2-aminobenzothiazole 3-oxide *IV* was isolated as a product of an electrolytical preparative reduction at a mercury cathode in 0.1M-HCl.

The aim of the present paper was an elucidation of the electroreduction of *o*-nitrothiocyanobenzene *I* at a mercury cathode, the isolation and identification of all products of such a reduction over a wide pH-region and over the whole area of reduction potentials, and an estimation of the possibilities of practical applications of the intramolecular chemical follow-up reactions occurring here.

## EXPERIMENTAL

## Starting and Model Substances

The *o*-nitrothiocyno derivative *I* was prepared according to a procedure described by Wagner-Jauregg and Helmert<sup>4</sup>. After a twice repeated sublimation *in vacuo* (4 Torr) obtained with an oil vacuum pump at 110–120°C and a crystallization from ethanol the yellowish needle-like crystals melted at 129.5–130°C in a capillary. The literature<sup>4,5</sup> gives 130°C and 132.5°C as melting points. The elemental analysis is in agreement with the theoretical values. The infra-red spectra of *I* prepared in this way, measured in CHCl<sub>3</sub> exhibit the following bands: 3300 cm<sup>-1</sup> (m), 3025 cm<sup>-1</sup> (m), 2160 cm<sup>-1</sup> (m), 1600 cm<sup>-1</sup> (m), 1535 cm<sup>-1</sup> (s), 1470 cm<sup>-1</sup> (m), 1345 cm<sup>-1</sup> (s). 2-Aminobenzothiazole *II* was prepared according to a procedure also published by the above authors<sup>4</sup>. The crude product was a yellowish substance, melting at 125–125.5°C in a capillary. After a purification on a column of silica gel a sample melting at 130.5–131°C resulted; this is in accordance with literature<sup>4</sup>. The preparation of 2-aminobenzothiazole 3-oxide *IV* was based on a procedure described by Liss<sup>6</sup>. An original pressure hydrogenation apparatus<sup>7</sup> has been constructed in which several hydrogenations of *I* were performed. After approx. 2 hours of hydrogenation 2 mol of hydrogen were consumed: this corresponds to the reductive transformation of *I* to the N-oxide *IV*. After filtering-off the Raney nickel a slightly yellow-coloured filtrate was obtained which yielded a dull white crystalline substance in part sublimating and in part melting with decomposition at temperatures higher than 145°C. The crude product was purified by chromatography on a poured silica gel column. In accordance with literature<sup>6</sup>, the crystals obtained in this manner melted at 185–186°C with decomposition.

For C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>OS (166.2): calculated: 50.58% C, 3.64% H, 16.86% N, 19.29% S; found: 49.56% C, 3.88% H, 16.28% N, 19.34% S. No figures were given for the elemental analysis of the base in the original paper<sup>6</sup>. The mass spectra obtained for this substance point to the formation of the molecular ion 166 *m/e* which agrees with the molecular weight of the N-oxide *IV*. The next prominent fragment has a mass of 150 *m/e* corresponding to the molecular weight of the 2-amine *II* formed on splitting-off 16 *m/e* corresponding to oxygen. The further prominent fragments are 123, 118, 108 and 96 *m/e*. The infra-red spectra of our substance-obtained by a potassium bromide technique — yield a diffuse band with a maximum at 3420 cm<sup>-1</sup> (s), further band at 3000 cm<sup>-1</sup> (w), 1575 cm<sup>-1</sup> (s) and 1430 cm<sup>-1</sup> (s). The electron spectra recorded with an ethanolic solution exhibit the following bands: λ 220 nm, ε 18000; λ 247 nm, ε 8400; λ 290 nm, ε 9620. In order to estimate the protonation of the amino group, electron spectra of the N-oxide *IV* were recorded with Britton–Robinson buffers containing 20% ethanol at 10<sup>-4</sup>M-N-oxide *IV* concentrations. By evaluating the absorption bands a value of 3.25 was obtained for p*K*. All spectral data point to the validity of the assumed structure.

The salts of the free base *IV*, *i.e.* its sulphate and hydrochloride, were prepared in order to characterize and to elucidate the structure of the N-oxide bond. The sulphate of *IV* was obtained by dissolving 50 mg of the free base in about 10 ml of distilled water and mixed with 3.4 ml approx. 0.1M-H<sub>2</sub>SO<sub>4</sub>. This solution was evaporated to dryness in a rotation vacuum still at 40°C and 15 Torr. The white amorphous substance, exhibiting an acid reaction on universal pH indicator paper, melted with decomposition in the range from 170°C to 172°C. Then it was again dissolved in ethanol and left standing upon CaO for about 2 hours. The filtered clear solution was again evaporated to dryness in a vacuum rotation still. The resulting product melted at 173.5–174.2°C with decomposition. For C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub> (264.2): calculated: 31.78% C, 3.05% H, 10.6% N, 24.2% S; found: 32.06% C, 3.25% H, 10.37% N, 23.9% S. One mol of sulphuric acid corresponds to one mol of the base. The preparation of the hydrochloride described in the quotations<sup>3,6</sup> was only repeated. The product obtained in this way had a m.p. 227–230°C with decom-

position. The papers<sup>3,6</sup> give m.p. 229–230°C. For  $C_7H_7N_2ClOS$  (202.6): calculated: 41.4% C, 3.46% H, 13.85% N, 15.85% S; found: 39.92% C, 3.27% H, 13.34% N, 16.39% S. As in case of the free base the elemental analysis of the hydrochloride is not satisfactory. In the original paper<sup>6</sup> the numerical values are not presented; they are given in the more recent paper by Lund<sup>3</sup> but the theoretical value for the carbon contents is erroneous. After correcting the calculation the found carbon contents<sup>3</sup> differ from the theoretical ones by about 0.5%. The mass spectra of the hydrochloride yield a molecular ion 203  $m/e$  and the fragments 166  $m/e$  and 150  $m/e$  characteristic both of the hydrochloride and of the free base. The discrepancy in the elemental analysis both of the base and of the hydrochloride are probably caused by the strongly polar structure of this substance. It is probable that in spite of the extremely careful chromatographic separation (twice column-separated) a slight quantity of some of the compounds accompanying *IV* is bound to it and passes the chromatographic column. Later it interferes in the elemental analysis.

*o*-Nitrothiophenol *X* was obtained in a procedure according to Foster and Reid<sup>8</sup>. Light yellow crystals of the product melted at 56–57°C. The literature<sup>8</sup> quotes 57–58°C. 2,2'-Diaminodiphenyl disulphide was also prepared according to Foster and Reid<sup>9</sup>. On crystallizing the crude product from water light yellow crystals resulted which melted at 93.0–93.5°C. A value of 93°C follows from the paper by Foster and Reid<sup>9</sup>. *o*-Aminothiophenol resulted in procedure described by Nys and van Dormael<sup>10</sup>. In a vacuum distillation of the crude product at 1.5 Torr a light yellow oily product passed over at 83.5–84°C. The paper<sup>10</sup> quotes 90–91°C at 3 Torr.

Ethanol for electrochemical measurements was prepared by treating commercial product with  $Ag_2O$  and CaO and rectifying it on column. The final drying operation of ethanol was performed by the molecular sieve Calsit 5, Type 5, produced by VÚRUP Bratislava. Dimethylformamide (denoted as DMF in the text) was dried with  $K_2CO_3$  and distilled in a vacuum still at a pressure of 10–20 Torr. For the electrochemical measurements we used the middle fraction. The Britton-Robinson buffers were prepared from analytical grade reagents and their pH-values were measured with a glass electrode making use of an electronic pH-meter. The chromatographic solvents were dried, treated and distilled according to the methods described in the literature<sup>11,12</sup>.

#### Instruments and Experimental Techniques

The polarographic investigations were performed with a LP 60 polarograph making use of a Kalousek cell with a separated saturated mercurous sulphate electrode. The polarographic capillary had the following characteristics:  $m = 1.9$  mg/s and  $t_1 = 4$  s in water at zero applied voltage. The oxygen was removed by bubbling through with nitrogen. The pH-values of the solutions were measured with a compensation pH-meter Radiometer PHM4C with a glass electrode. The Kalousek commutator was made in the workshops of this Institute. The mass spectra were measured with an LKB 9000 apparatus. The electron spectra were obtained with a Unicam SP 800, the infrared spectra with a Zeiss UR 10.

The samples of all substances for elemental analysis were dried on  $P_2O_5$  in the vacuum of an oil pump. The temperatures of the melting points were not corrected. The concentrations of organic solvents are expressed in volume percents.

The coulometric measurements were performed with an electronic integrator Amel 558/RM. The decrease in the concentration of the substance during electrolysis was followed polarographically directly in the electrolysis cell. The values of  $n$  were corrected by subtracting from the total consumed charge the charge consumed at the same potential during the same period of time but electrolyzing the solution of the supporting electrolyte alone. In coulometry with a stationary mercury pool electrode the surface of which is not renewed the mercury layer on the bottom of the micro cell served as a cathode with a surface area of about 0.5  $cm^2$ ; the anode was a saturated

mercurous sulphate electrode. The currents at the beginning of the electrolysis amounted to about 70–90  $\mu\text{A}$ . The constant-potential electrolyses were performed with a polarograph as a voltage source without IR compensation. During electrolysis the stirring was effected by a stream of inert gas. The correctness of the values thus obtained was verified by coulometry of a  $5 \cdot 10^{-4}\text{M}$ - $\text{Cd}^{2+}$  solution in approx.  $0.01\text{M-HClO}_4$ . The coulometric measurements during preparative electrolyses at stirred large-area mercury-pool electrodes were carried out in a similar manner.

The controlled-potential preparative electrolysis at a large-area mercury electrode was performed in an all-glas cell<sup>1,3</sup>. The solution contained a  $1.0\text{--}2.5 \cdot 10^{-3}\text{M}$  solution of depolariser and the maximum volume of this solution was 200 ml. Both the solution and the mercury-pool electrode were stirred by a two-arm stirrer at a rate of 1490 revs/min. The anodes were platinum wires with areas comparable with the cathode area, immersed in  $0.1\text{M-H}_2\text{SO}_4$  or in a saturated solution of  $\text{Na}_2\text{SO}_4$ . The cathode compartment was deaerated by passing a stream of nitrogen through the solution. For electrolyses where the value IR did not exceed 10 V a potentiostat of the Southern Analytical Company was used. In all other cases, the electrode potential was controlled manually making use of a circuit containing an adjustable dc. source Tesla BM 208 and the potential of the working cathode was checked by an electronic voltmeter Tesla BM 289. The concentration changes during electrolysis were followed polarographically. A coulometric integrator was inserted in the circuit. The electrolysis lasted until the current decreased below 1% of the starting value. If the residual current remained higher a correction of the coulometric measurement was made by electrolyzing a blank solution.

The solution after electrolysis was treated like this: It was always neutralized to pH 6–7 and then evaporated to dryness in a vacuum rotation still. The rest was extracted with absolute ethanol at room temperature and at stirring. The inorganic salts were filtered off and extracted in the flask with several more portions of absolute ethanol. The individual portions of the pure extract were combined, concentrated *in vacuo* and after preliminary chromatographic analysis on a thin layer separated on a suitably prepared chromatographic column (silica gel Silpearl, Kavalier, Czechoslovakia). The fractions obtained by eluting the chromatographic column were analysed again by thin-layer chromatography (Silufol, Kavalier). The detection of the spots was made by iodine vapours. The solutions resulting from the electrolysis under polarographic conditions (26–30 hours duration) were also analysed by means of thin-layer chromatography. The reduction products were treated as above.

## RESULTS AND DISCUSSION

### *Polarography of o-Nitrothiocyanobenzene*

Fig. 1 demonstrates a  $E_{1/2} = f(\text{pH})$ -plot for the *o*-nitrothiocyano derivative *I* in Britton–Robinson buffers containing 50% ethanol. The polarographic behaviour was followed over the range from  $0.5\text{M-H}_2\text{SO}_4$  to pH 9.0. In this region *I* is stable, at pH > 9 a hydrolytic fission takes place. The products of the hydrolysis, cyanides and *o*-nitrothiophenol *X*, the latter immediately oxidizing to the yellow-coloured 2,2-dinitrodiphenyl disulphide *XI*, were polarographically detected in alkaline media making use of a standard addition. It follows from the electron spectra that at pH 9.2 50% of substance *I* undergoes a hydrolytic fission within 10 minutes. The papers<sup>1,3</sup> do not mention this hydrolytic fission. In accord with the above authors<sup>1,3</sup> three cathodic waves in acid media  $0.5\text{M-H}_2\text{SO}_4$  were found. As all cathodic waves of *I* at

any pH value they are diffusion-controlled. The ratio of wave-heights of the three cathodic waves is 4.0 : 0.9 : 1.3. With increasing the acid concentration above 0.5M the second cathodic wave changes into a maximum. This can be suppressed by adding 0.01% of gelatin but this also results in simultaneous suppressing the most negative wave. Over the pH-range from 1.5 to 5.0 a single cathodic wave can be only seen the height of which is approximately the same as that of the first wave in strongly acidic media and is pH-independent (Fig. 2). Between pH 5.0 and 9.0 the formation of two and then of three waves can be observed. The authors<sup>1,3</sup> arrived at the same conclusion but they did not study in detail the influence of pH on  $E_{1/2}$  of the waves. Our finding that  $E_{1/2}$  of both the second and of the third cathodic wave is pH-independent between pH 6.0 and 9.0 is rather important. It points to the independence of the primary electron transfer on hydroxonium ion concentration this being typical for the reduction of a thiocyanate group<sup>17,18</sup>. On the other hand, the height of the first

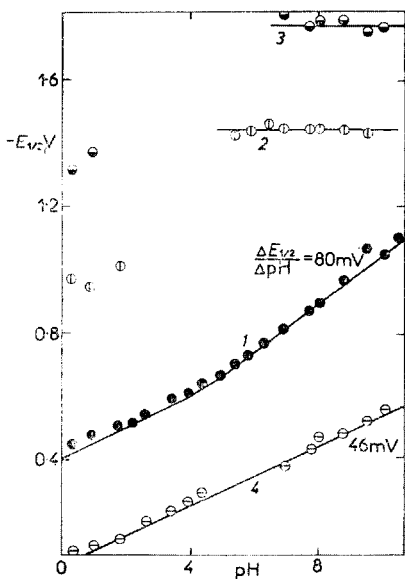


FIG. 1

Dependence of  $E_{1/2}$  on pH for Polarographic Curves of  $5 \cdot 10^{-4}$  M Solutions of the Nitro Derivative I in Britton-Robinson Buffers Containing 50% Ethanol

1 First cathodic wave; 2 second cathodic wave; 3 third cathodic wave; 4 anodic wave on the commutated curve.

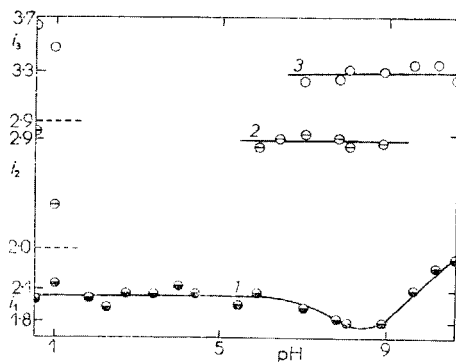


FIG. 2

Dependence of the Wave-Height of Polarographic Waves on pH of  $5 \cdot 10^{-4}$  M Solutions of the Nitro Derivative I in Britton-Robinson Buffers Containing 50% Ethanol

1  $i_1$  First cathodic wave, 2  $i_2$  second cathodic wave, 3  $i_3$  third cathodic wave.

cathodic wave (the half-wave of which is a linear function of pH) is pH-independent up to pH 6 and slightly decreases between pH 6 and 9 (Fig. 2).

The investigation of commutated curves (discontinuously changed square-wave voltage) gave a single anodic wave with auxiliary potentials  $E_{aux}$  corresponding to all three cathodic waves at all pH-values. The anodic wave already resulted with  $E_{aux}$  corresponding to the limiting current of the first wave. Fig. 1 demonstrates the change of its  $E_{1/2}$  with pH. If  $E_{aux}$  corresponds to the limiting currents of the second or third wave,  $E_{1/2}$  of the commutated anodic wave only shifts to more negative values. The commutated anodic wave can be ascribed to the reversible oxidation of the NHOH group, formed in the four-electron reduction of the nitro group of *I*, to an NO group at the potential of the first cathodic wave.

### Coulometry

The results of a detailed coulometric investigation of *I* at different pH-values and at different reduction potentials are shown in Table I. In 0.5M- $H_2SO_4$  the values of  $n$  obtained by coulometry both at polarographic conditions (with 20% DMF) and in electrolysis at a large-area mercury electrode are equal. After a long-term electrolysis of *I* in this media different products were isolated according to the potential of electrolysis. Thus, at the potential of the first cathodic wave where  $n = 4$  follows from coulometric measurements the N-oxide *IV* and 2-amine *II* were isolated as products and identified by comparing their chromatographic behaviour with authentic samples.

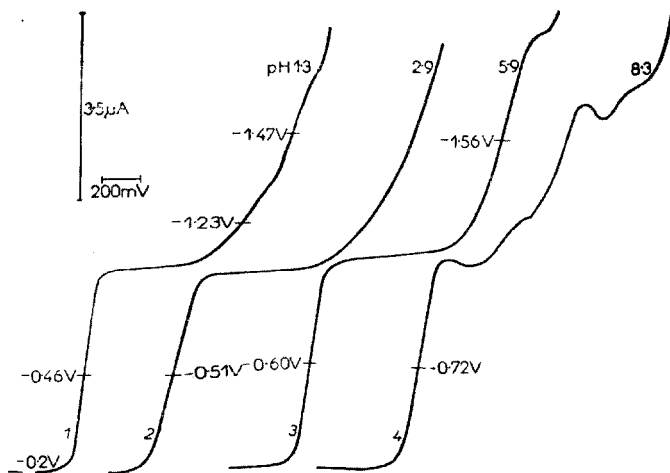


FIG. 3  
Polarographic Curves of  $5 \cdot 10^{-4}$  M Solutions of the Nitro Derivative *I* in Britton-Robinson Buffers Containing 50% Ethanol

It is somewhat surprising that two different products are formed here; the ratios of their quantities cannot be estimated from these experiments; their formation, however, can account for the non-integer values of  $n > 4$ . If the polarographic electrolysis occurred at more negative potentials in the region of the second wave, the same products were isolated but the value of  $n$  increased. One can therefore assume that at potentials of the second cathodic wave mainly a further reduction of  $-\text{NHOH}$  to  $-\text{NH}_2$  occurs. Finally, in electrolysis at the most negative potentials corresponding to reduction in the third wave, 2,2'-diaminodiphenyl disulphide was isolated in addition to the N-oxide *IV* as an oxidation product of *o*-aminothiophenol *VI* during its isolation. The value of  $n$  (Table I) changes with the degree of depletion of *I* from the solution during electrolysis; a higher value of  $n$  corresponds to a higher degree of depletion. It can be concluded that a substance results in the system under these conditions which is very reactive and easily oxidizable most probably *o*-aminothiophenol. Anyway, both the high value of  $n$  and the formation of a disulphide confirm a reductive splitting of the SCN group in this region. The coulometric measurements performed during polarographic electrolysis of solutions with 0.4 to 3M- $\text{H}_2\text{SO}_4$  at potentials corresponding to the limiting current of the second polarographic wave passing into a maximum demonstrated that the value of  $n$  does not vary to any greater extent since it only fluctuates between 4.7 and 4.9. A difference can be only seen in the rate of electrolysis which in 3M- $\text{H}_2\text{SO}_4$  is considerably lower than in 0.5M- $\text{H}_2\text{SO}_4$ . Evidently, no comparison of our coulometric results with those of the authors<sup>1,3</sup> can be made because their data are only approximate and rather scarce. The finding of the N-oxide *IV*, of the 2-amine *II* and of 2,2'-diaminodiphenyl disulphide as products of a long-time polarographic reduction in the pH region from 1.5 to 5.5 point to a more complicated reaction course with participation of chemical follow-up reaction. At pH 5.5 to 8.5 where gradually two and finally three cathodic waves can be observed, the N-oxide *IV*, 2,2'-diaminodiphenyl disulphide and traces of the 2-amine *II* have been found regardless of the applied reduction potential (corresponding to the limiting currents of any of the three cathodic waves). The coulometric results obtained in electrolysis at potentials corresponding to the limiting currents of the first, second and third wave, respectively, differ, however, in principle. As follows from Table I, they do not give integer values of  $n$  which would perhaps enable us to ascribe the waves unambiguously to a certain electrode process. In electrolyses at the most negative potentials where the third wave appears the coulometric value of  $n$  again increases with the duration of electrolysis.

### *Preparative Electrolyses*

After a preparative electrolysis with 0.5M-HCl as supporting electrolyte different products were isolated according to the chosen electrode potential (Table II). From coulometric measurements (Table III) and from the ratios of products isolated from

the electrolyte after electrolysis at potentials over the region of the first and of the second cathodic wave in these media, a 4-electron reduction of the nitro group follows for the first wave and at potentials of the second wave an overall 6e-reduction to the corresponding amino derivative. During these electrolyses the electrolyte underwent an intense yellow-green coloration; the most intense coloration was observed at a 50% conversion of the starting material, *I*. Towards the end of the electrolysis the colour disappeared again. On polarograms recorded during electrolysis a simultaneous decrease in the height of all three cathodic waves was observed. In electrolyses where the reduction potential is preset on a value corresponding to the foot, to the half-wave potential or to the limiting current of the third wave, an anodic wave appears on the control polarograms; its formation points to a reduction of the thiocyanate group and corresponds to an anodic reaction of the mercapto derivative *VI* thus formed. By oxidation after electrolysis with air the anodic wave disappears and a cathodic wave is formed which corresponds to the reduction of the disulphide *V* resulting in the electrooxidation. During electrolysis of this yellow solution at the potential of the limiting current of the cathodic wave of the disulphide *V*, the solution becomes colourless again and the polarogram reveals two anodic waves characteristic<sup>7</sup>

TABLE I

Coulometric Measurements Performed During Polarographic Electrolysis and Electrolysis at a Large Area Mercury Electrode

All pH values given here are referred to buffers containing 50% ethanol.

Media	Polarographic electrolysis		
	Applied potential $V^a$	Value of $n$ $e$	Electrolysis performed up to
0.5M-H <sub>2</sub> SO <sub>4</sub> , 20% DMFA	-0.6	3.95	62%
	-1.2	4.65	56%
0.1M-H <sub>2</sub> SO <sub>4</sub> , 20% DMFA	-0.6	3.90	47%
	-1.3	5.35	59%
	-1.5	4.7/6.2	40/62%
pH 2.50	-0.9	4.0	50%
	-1.2	4.30	68%
	-1.4	3.90	60%
pH 3.55	-1.0	4.10	60%
pH 4.47	-0.8	4.65	80%
pH 4.64	-1.2	4.30	80%
	-1.6	3.75	68%

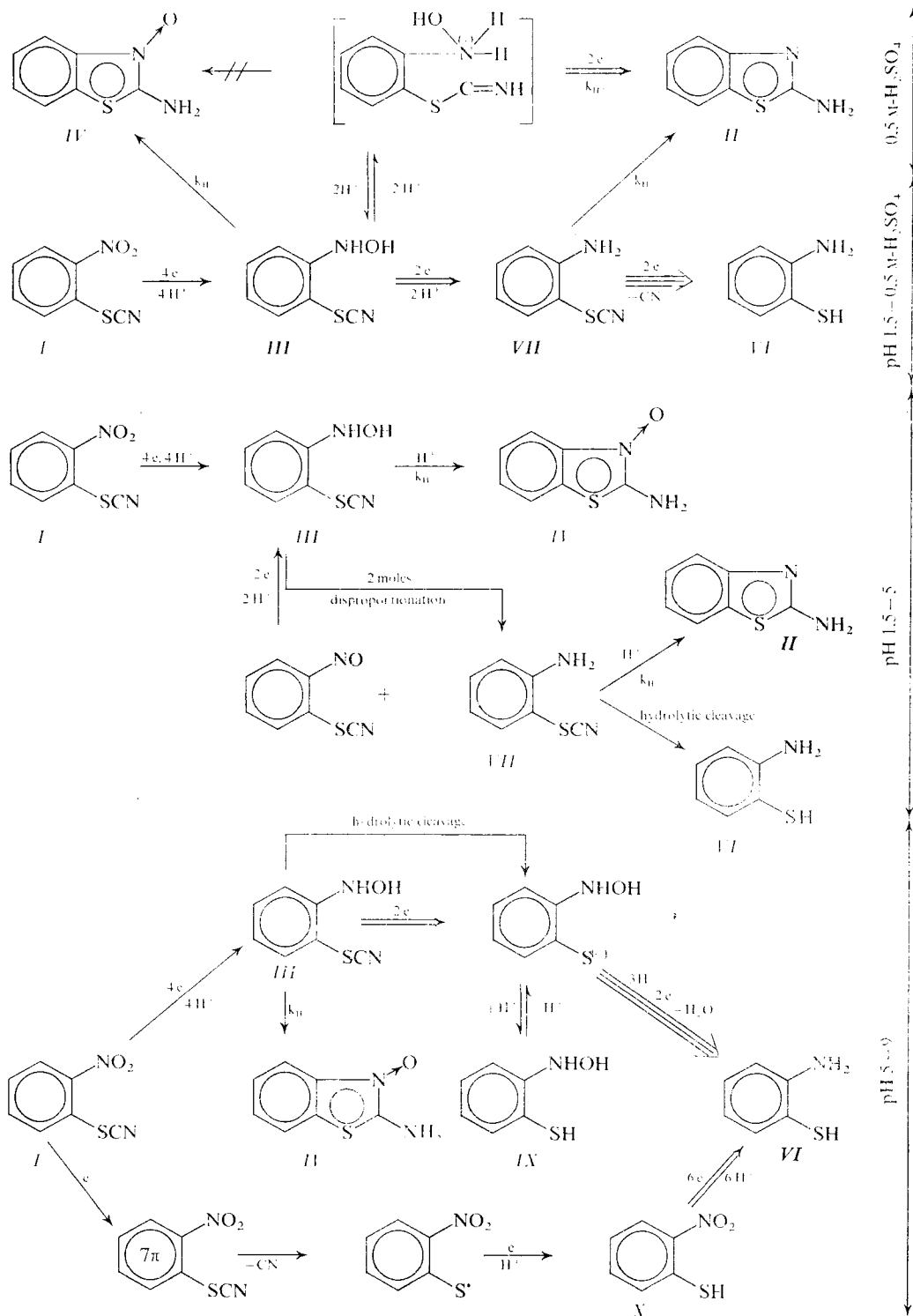


TABLE I  
(Continued)

Media	Electrolysis at a large area mercury electrode		
	Applied potential $V^a$	Value of $n$ $e$	Electrolysis performed up to
0.5M-H <sub>2</sub> SO <sub>4</sub> , 40% ethanol	-0.7	4.30	52%
	-1.1	5.10	58%
	-1.2	4.55	76%
	-1.3	4.60	66%
	-1.4	4.55	54%
	-1.5	5.7/6.6	35/54%
	-1.6	6.0	58%
pH 2.35	-0.9	4.0	50%
	-1.2	4.30	68%
	-1.4	3.90	60%
pH 3.55	-1.0	4.10	60%
pH 4.47	-0.8	4.65	80%
	-1.2	4.30	80%
	-1.6	3.75	68%
pH 5.51	-0.8	3.95	75%
pH 6.45	-1.0	4.15	80%
	-1.5	4.10	82%
	-1.9	5.60	70%
	-2.1	4.0/5.0	40/60%
pH 6.7	-1.3	4.30	55%
	-1.5	4.30	80%
pH 7.1	-1.2	5.50	53%
	-2.1	4.0/5.0	40/70%

<sup>a</sup> The values of potentials applied in the electrolyses can be taken from Fig. 3 where the polarograms showing the studied pH values are referred to a mercurous sulphate electrode are demonstrated.

of the mercapto derivative VI. The Table II shows the yields of products isolated from this electrolyte after electrolysis which also points to a reductive cleavage of the thiocyanate group. In Table III the values of  $n$  obtained from coulometric measurements carried out during preparative electrolyses are compared to the  $n$  values calculated from the quantities of isolated products and from the theoretical electron



SCHEME 1

consumptions. All theoretical, calculated values of  $n$  for an electrolysis in 0.5M-HCl are in a good accord with the experimental coulometric values. The third cathodic wave corresponds to the 2-electron cleavage of the SCN-group (Scheme 1).

By electrolysing *I* in Britton-Robinson buffers at pH 1.5–4.5 the above products were also obtained but in different proportions (Table II). During electrolysis the height of the single cathodic wave decreases in agreement with depleting the depolariser solution; nevertheless, no anodic wave results. In the 4-electron reduction of the nitro group an unstable hydroxylamino intermediate *III* is formed which is prevalently deactivated in an intramolecular reaction giving rise to the N-oxide *IV*; in an intermolecular disproportionation<sup>7</sup> it can yield the amino derivative *VII*. The latter is deactivated in an intramolecular cyclisation with the formation of the amine *II*; to a certain degree a hydrolytic cleavage of the thiocyano group occurs giving rise to the mercapto derivative *VI* (Table II). The values of  $n$  calculated from the yields and the amount of electricity consumed are in a fair agreement with the coulometrically measured values over this pH region.

In electrolysis at pH > 5 where the second reduction wave develops mixtures of different composition as regards the above products, the mutual proportion being a function of the reduction potential. If the electrolysis is carried out at the potential corresponding to the region of the limiting current of the first cathodic wave the reaction mixture contains particularly the N-oxide *IV* (Table II); at the same time the percentage of the mercapto derivative *VI* increases with increasing pH. During electrolysis the height of both cathodic wave decreases and the anodic wave of the mercapto derivative *VI* gradually develops. The solution turns yellow during this process, this colouration disappears, however, as soon as all the nitro derivative *I* has been exhausted. The mercaptan *VI* is also formed in electrolysis where the electrode potential is set to a value corresponding to the first cathodic wave; this gives evidence about the fact that in a part of the hydroxylamino intermediate *III* a hydrolytic fission of the S—C bond in the SCN group occurs. One can assume that the mercapto derivative *IX* or *VI* is oxidised by the other components of the system to the yellow disulphide *V* and causes thus that the solution turns yellow during electrolysis. The cyanides set free during this hydrolysis could not be unambiguously detected by polarography. The presence of a considerable amount of aminothiophenol *VI* among the products both at the potentials of the first and of the second wave at pH 5.5–6.0 points not only to a reduction and to hydrolytic cleavage of the SCN group but also to a reduction of the nitro group to an amino group. This 6-electron reduction occurs even if the pH of the solution does not enable the protonation of the hydroxylamine group<sup>14</sup>. Since no azoxy derivatives have been observed or detected their formation is rendered difficult by steric reasons and by the intramolecular cyclisation a mechanism of reduction *via* these compounds cannot be taken into account. Considering that in the system *o*-hydroxylaminothiophenol *IX* results which easily eliminates water under formation of an *o*-quinoid sulphimine arrangement (Scheme 1), one can

TABLE II

Results of Preparative Electrolysis of  $2.5 \cdot 10^{-3}M$  Solutions of Substance *I* (90 mg) with 50% Ethanol at Different pH Values

Media	Applied potential V	Initial current mA	Final current mA	Products of electrolysis
0.5M-HCl	-0.6 <sup>a</sup>	175	2	73 mg N-oxide <i>IV</i> 4 mg amine <i>II</i> 5 mg disulphide <i>V</i>
	-1.4 <sup>b</sup>	250	28	45 mg N-oxide <i>IV</i> 28 mg amine <i>II</i> 2 mg disulphide <i>V</i>
	-1.6 <sup>c</sup>	260	33	43 mg N-oxide <i>IV</i> 9 mg amine <i>II</i> 28 mg disulphide <i>V</i>
pH 2.97	-1.2	260	2	50 mg N-oxide <i>IV</i> 23 mg amine <i>II</i> 2 mg disulphide <i>V</i>
pH 3.5	-1.2	200	2	53 mg N-oxide <i>IV</i> 13 mg amine <i>II</i> 7 mg disulphide <i>V</i>
pH 5.62	-1.6 <sup>a</sup>	300	2	47 mg N-oxide <i>IV</i> 8 mg amine <i>II</i> 28 mg disulphide <i>V</i>
	-2.1 <sup>b</sup>	330	34	5 mg N-oxide <i>IV</i> 57 mg disulphide <i>V</i>
pH 6.8	-1.4	295	2	30 mg N-oxide <i>IV</i> 40 mg disulphide <i>V</i>
pH 6.63	-2.1	330	74	4 mg N-oxide <i>IV</i> 57 mg disulphide <i>V</i>
pH 8.0	-1.6 <sup>b</sup>	270	8	20 mg N-oxide <i>IV</i> 44 mg disulphide <i>V</i>
	-2.1 <sup>c</sup>	215	34	34 mg N-oxide <i>IV</i> 38 mg disulphide <i>V</i>
pH 8.9	-1.1 <sup>a</sup>	180	6	18 mg N-oxide <i>IV</i> 47 mg disulphide <i>V</i>
	-1.5 <sup>b</sup>	250	8	25 mg N-oxide <i>IV</i> 45 mg disulphide <i>V</i>
	-2.1 <sup>c</sup>	215	—	12 mg N-oxide <i>IV</i> 51 mg disulphide <i>V</i>

<sup>a</sup> Applied potential corresponding to the limiting current of the first cathodic wave; <sup>b</sup> to that of the second cathodic wave; <sup>c</sup> to that of the third cathodic wave.

assume that this electroactive species is reduced with an uptake of 2 electrons with no participation of protons. The electroreduction can thus proceed regardless of the pH value of the solution. *o*-Hydroxylaminothiophenol *IX* may be formed in a chemical hydrolytic fission of the hydroxylamine intermediate *III* because the reduction of the nitro group to NHOH lowers the pH range in which the fission of the thiocyanate group of *III* takes place as compared to the original nitro derivative *I*.

Over the pH region from 6.5 to 9.0 where *I* gives three cathodic waves the N-oxide *IV* and the mercapto derivative *VI* are always obtained regardless of the potential of the electrolysis. A prewave appears during the electrolysis which precedes the first cathodic wave; its half-wave potential only slightly differs from that of the main wave. Immediately after starting the electrolysis the colour of the electrolyte, originally colourless, turns yellow. The height of all four cathodic waves decreases and the anodic wave of the mercapto derivative *VI* appears. The proportion of the N-oxide sinks with

TABLE III

Results of Coulometry During Preparative Electrolysis of  $2.5 \cdot 10^{-3}$  M Solutions of Substance *I* Containing 50% Ethanol in Buffers of Different pH

Media	Applied potential V	$n^d$	$n^e$	$n^f$
0.5M-HCl	-0.6 <sup>a</sup>	4.45	4.35	4.40
	-1.4 <sup>b</sup>	4.65	4.70	4.70
	-1.6 <sup>c</sup>	6.40	6.45	6.50
pH 2.9	-1.2	4.50	4.50	4.65
pH 3.5	-1.2	4.50	4.40	4.40
pH 5.6	-1.6 <sup>a</sup>	6.50	6.55	7.20
	-2.1 <sup>b</sup>	7.60	5.40	5.20
pH 6.8	-1.4	6.60	6.75	6.60
pH 6.6	-2.1	7.55	5.45	5.10
pH 8.0	-1.6 <sup>b</sup>	6.70	6.65	6.70
	-2.1 <sup>c</sup>	6.50	5.70	5.70
pH 8.9	-1.1 <sup>a</sup>	7.0	—	6.90
	-1.5 <sup>b</sup>	7.0	7.0	6.40
	-2.1 <sup>c</sup>	7.20	6.40	6.0

<sup>a</sup> Applied potential corresponding to the limiting current of the first cathodic wave; <sup>b</sup> to that of the second cathodic wave; <sup>c</sup> to that of the third cathodic wave. <sup>d</sup> Calculated from the mass balance of isolated products; <sup>e</sup> determined at total electrolysis; <sup>f</sup> obtained from the plot *C* vs *Q*.

increasing pH values (Table II) which is in accord with the conception of an acid catalysed intramolecular interaction.

The explanation of the formation of the mercapto derivative *VI* in considerable quantities already at potentials of the first wave assumes that the radical anion formed in the primary step of 4-electron reduction of the nitro group splits of a  $\text{CN}^-$  with the formation of a neutral radical  $\text{O}_2\text{NC}_6\text{H}_4\text{S}^\bullet$ ; this happens in agreement with the mechanism suggested by Bartak and coworkers<sup>16</sup>. The radical takes up a further electron and gives a *o*-nitrothiophenoxide ion (Scheme 1). This means that with *I* in neutral and slightly alkaline media the reductive splitting of  $\text{SCN}^-$  precedes the reduction of the nitro group. The resulting *o*-nitrothiophenol *X* is reduced — this follows from our experience<sup>7</sup> — in a single 6-electron wave in neutral and slightly alkaline media. The half-wave potential of this cathodic wave is almost identical with the half-wave potential of the second wave given by the substance *I* in this media. Basing on this and on an addition of *X* to the solution of *I* in d.c. polarographic experiments at pH 6.5–8.5 one can conclude that the substance *X* resulting from the reduction of *I* at potentials of the first wave (a 4-electron reduction) is further reduced to *VI* at potentials of the second cathodic wave. The third, most negative wave in neutral and slightly alkaline solutions can be ascribed to the electroreduction of the substituted hydroxylamine *IX* (Scheme 1) which is a product of the hydrolytic fission of the intermediate *III*. As described above this is reduced without proton participation. In this media, too, an agreement between the experimental values of *n* and those obtained from the substance balance can be observed.

#### *Suggested Scheme for the Electroreduction Mechanism of o-Nitrothiocyanobenzene*

Since neither the *pK* values of the electroactive groups in the starting material *I* have been accurately determined nor those in the intermediates of electrolysis, all protonation reactions of these substances are not given in this Scheme 1. However, it is evident that preceding protonations play a role, in particular in the reduction of the nitro group. A simple arrow denotes in the scheme electrode processes taking place at the potentials of limiting current of the first wave, a double arrow those in the region of the second cathodic wave, and a triple arrow denotes the electrode processes occurring at the potentials of the limiting current of the most negative wave.

The investigation revealed that the course of the electroreduction of *o*-nitrothiocyanobenzene is complicated. It seems that the authors<sup>3</sup> underestimated the rate and the extent of the intramolecular cyclisation interaction. In fact, this reaction is very fast and plays a role even in dc. polarography. The conviction of some investigators<sup>1</sup> about the independence of the nitro group reduction of the thiocyanate group and *vice versa* showed to be quite erroneous with the *ortho* derivative *I*. The tendency of the thiocyno group to a hydrolytic fission, as well as the effect of this group as an

*ortho* substituent on the protonation equilibrium of the nitro group and the course of the chemical intramolecular cyclisation cause an anomalous reaction mechanism.

The conception of an acid catalysis of the follow-up reaction between the —SCN and —NHOH group is supported by the optimum 88% yield of the N-oxide *IV* in electrolysis with controlled potential in 0.1M-HCl as supporting electrolyte. Classical chemical reductions and the catalytic hydrogenation of *I* do not lead to such a yield of the N-oxide. Consequently, one can expect that suitable application of this reaction type to some other systems will lead to novel, interesting substances in high yields.

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