

## THE NITROPRUSSIDE ION REDUCTION PRODUCTS\*

J. MAŠEK and E. MÁŠLOVÁ

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 118 40 Prague 1*

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Products of one-, two- and four-electron reduction of the nitroprusside ion were prepared electrolytically and studied by electrochemical methods and absorption spectra. The products undergo various spontaneous and mutual reactions which are described and on their basis the over-all mechanistic reduction pattern is derived. Among the most important reactions of this kind belongs the disproportionation of the one-electron reduction product and the transformation of the two-electron reduction product to the linkage isomer  $[\text{Fe}(\text{CN})_4(\text{NC})\text{NO}]^{4-}$  with one N-bonded cyanide group.

In Parts IV and V of this series<sup>1,2</sup> the nitroprusside ion reduction mechanism was studied at the mercury dropping electrode, *i.e.* with electrolysis times of approximately 3 s. Under these conditions it was possible to follow rapid volume reactions of the primary products occurring during the drop time and from the results a mechanistic reduction pattern was derived which is valid for the electrolysis with the mercury dropping electrode. Experiments with the mercury hanging drop electrode indicated, however, that certain reduction products undergo volume reactions with longer half-life periods which could not be followed polarographically.

In order to obtain information about the behaviour of the nitroprusside ion reduction products in the time period up to several hours, *i.e.* under conditions of the usual chemical work, bulk electrolyses were performed at large-area electrodes and the products were followed by electrochemical methods and absorption spectra. The corresponding results are reported in the present paper.

## EXPERIMENTAL

The large-area electrolyses were performed with mercury-pool electrodes in a cell containing a separated standard calomel reference electrode (s.c.e.), separated graphite electrode in 1M- $\text{Na}_2\text{SO}_4$  as counter anode, a mechanical stirrer and the mercury dropping electrode. During the electrolyses the potential applied to the mercury-pool electrode was controlled with the potentiostat Jaisle 1000 T using the three-electrode system and the solution was stirred. In certain stages of electrolysis the stirring was stopped, (in comparison experiments carried out to exclude the possible influence of a prolonged contact of the examined solution with metallic mercury the mercury was

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removed from the vessel into the reservoir with which the mercury pool was connected) and polarographic or voltammetric curves were recorded or samples for spectroscopy were taken. Polarographic and voltammetric experiments were performed with a three-electrode system. The polarograph LP 60 was used in connection with an *iR*-drop compensator. The voltammetric device designed in this Institute had the scan rate adjustable up to 333 V/s and contained a positive-feedback potentiostat. The voltammetric curves were recorded with the storage oscilloscope Tektronix 5103 N. The solutions were deaerated by nitrogen purified by passing through a BTS catalyst column. All chemicals were purity grade Lachema products.

## RESULTS

The nitroprusside ion is reduced polarographically in three waves. The first two each correspond to a reversible 1-electron reduction whereas in the third wave two electrons (or better, measured from the limiting current of the first wave, three electrons) are irreversibly consumed<sup>1,2</sup>. The first wave attains in the pH range 4–9 its full height corresponding to a 1-electron uptake whereas the heights of the second and third wave undergo with pH certain changes since the nitroprusside ion is reduced by two different mechanisms according to the pH value of the medium. The orientation experiments have shown that the electrolytic products are most stable at higher pH values. Therefore the fundamental electrolyses were carried out in the pH range 8–9 and only subsequently the behaviour of the system at lower pH values was investigated.

### *Electrolysis at Potentials of the Limiting Current of the First Wave (1-Electron Reduction)*

At pH 8.8 the height of the second wave is lower than corresponds to a 1-electron uptake whereas the height of the third wave measured from the limiting current of the first wave attains its full height corresponding to the uptake of 3 electrons (Fig. 1, curve 1; loc. cit.<sup>1</sup>, Fig. 7). When electrolyzing at potentials of the limiting current of the first wave in a Britton–Robinson buffer of pH 8.8 an anodic wave with  $E_{1/2}$  corresponding to the first wave (*I*) and cathodic waves *II* and *III* are obtained (Fig. 1, curve 2). This behaviour is in accordance with the former findings<sup>1,2</sup> that the electrode process in the first wave is reversible. After completing the electrolysis the corresponding anodic wave has the same height as the cathodic wave *I* before electrolysis, the wave *II* is by 15–20% higher and the wave *III* measured now from the zero line of the current is by about 7% lower than before electrolysis (the values of these changes show a considerable scatter depending on the time of electrolysis which changes with the conditions of the electrolysis).

After the electrolysis the solutions were examined polarographically in time intervals ranging from several minutes to several hours under the following conditions: *a*) standing under N<sub>2</sub> atmosphere in the electrolytic vessel with applied potential of electrolysis (without stirring), *b*) the same as *sub a*) with disconnected electrolytic circuit, *c*) the same as *sub a*) without contact with metallic mercury, *d*) passing

purified nitrogen or argon, *e*) passing hydrogen, *f*) passing ethylene through the solution. In all cases within several tens of minutes the anodic wave *I* shifted gradually to the cathodic side and the height of this anodic-cathodic wave decreased. At the

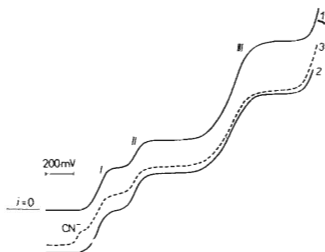


FIG. 1

Potentiostatic Electrolysis of the Nitroprusside Ion at Potentials of the Limiting Current of the Wave *I*

Phosphate buffer pH 8.8;  $10^{-3}$  M- $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ ; from 0.0 V (SCE). *1* Before electrolysis; *2* after electrolysis on passing 1 F/mol; *3* conditions as with curve 2 on standing under nitrogen for 40 min.

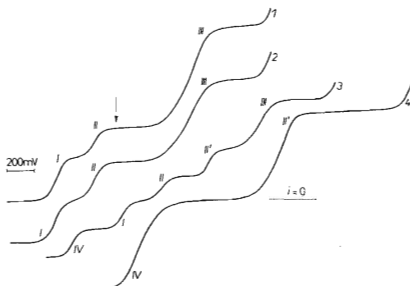


FIG. 2

Potentiostatic Electrolysis of the Nitroprusside Ion at Potentials of the Limiting Current of the Wave *II* at High pH

Phosphate buffer pH 8.8;  $10^{-3}$  M- $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ ; from 0.0 V (SCE); the arrow indicates the electrolysis potential. *1* before electrolysis; *2–4* after electrolysis on passing 2, 1.5, 2 F/mol.

same time a new anodic wave appeared with the half-wave potential by about 150 mV more positive than that of the wave *I*. This new wave was identified as due to free  $\text{CN}^-$  ions and hence it can be concluded that simultaneously a partial decomposition of the product under splitting off the cyanide ions occurs. With proceeding reoxidation the height of the cathodic waves *II* and *III* slightly decreases (Fig. 1, curve 3). When passing oxygen (air) through the solution of the reduction product the reoxidation is also observed, however, no free  $\text{CN}^-$  ions are split off. In this case the reoxidation proceeds within several seconds and after the reoxidation is completed all three waves have the same height as before the electrolysis.

At lower pH values (7.3–4.0) after the electrolysis the anodic wave corresponding to the first wave also appears but its height is smaller than that of the first wave before electrolysis. At the same time the cathodic waves *II* and *III* are slightly lower than before electrolysis. The decrease of all waves is more pronounced with lowering the pH value. By standing at these lower pH values again the cathodic part of the wave *I* is slowly developed and at the same time the height of all three waves slightly decreases. A similar behaviour is observed when the reoxidation is carried out by air.

#### *Electrolysis at Potentials of the Limiting Current of the Wave II*

When electrolyzing at potentials just after reaching the limiting current of the wave *II* at pH 8.8 then up to the charge consumption of  $1F$  per mol of the nitroprusside ion exactly the same pattern is obtained as when the electrolysis is performed at potentials of the limiting current of the wave *I* (Fig. 2, curve 2). After surpassing  $1F/\text{mol}$  the wave *II* is decreased, however, its anodic part does not develop even though this wave is polarographically reversible. The anodic wave *I* is decreased and a new anodic wave *IV* is formed with the half-wave potential 0.0 V vs SCE, the height of which is the double of the decrease of the anodic wave *I*. At the cathodic side a new wave *II'* is formed with the half-wave potential  $-1.0$  V vs S.C.E. and at the same time the wave *III* decreases (Fig. 2, curve 3). When reaching  $2F/\text{mol}$  the waves *I*, *II* and *III* disappear and only the cathodic wave *II'* and the anodic wave *IV* are left on the polarogram, both of which have the same height corresponding to 2-electron reactions (Fig. 2, curve 4). At pH 7.3 and lower the pattern is similar as at pH 8.8 but during the electrolysis also the wave corresponding to free  $\text{CN}^-$  ions appears on the polarogram. In the final stage of electrolysis in addition to this wave the curve shows the anodic wave *IV* and the cathodic wave *II'* which are at these pH values lower than corresponds to the exchange of 2 electrons (Fig. 3, curve 2). With a further decrease of the pH value of the electrolyzed solution the resulting waves *IV* and *II'* are diminished and at pH < 6 these waves are not observed. A subsequent increase of the pH value after the electrolysis does not cause a development or increase of these waves to the 2-electron height observed when the electrolysis is performed at pH > 8.

By air-oxidation the original nitroprusside waves *I*, *II* and *III* appear and the waves

*IV* and *II'* disappear. In the final stage of this reoxidation the waves *I*, *II* and *III* attain the same height as before the electrolysis but at pH 7.3 and lower the anodic wave due to  $\text{CN}^-$  ions is left on the polarogram and the cathodic waves *I*, *II* and *III* are lower

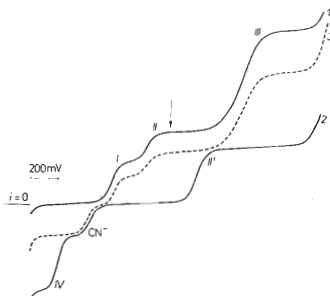


FIG. 3

Potentiostatic Electrolysis of the Nitroprusside Ion at Potentials of the Limiting Current of the Wave *II* at Lower pH

Phosphate buffer pH 7.3;  $10^{-3}\text{M-Na}_2\text{Fe}(\text{CN})_5\text{NO}$ ; from 0.0 V (SCE); the arrow indicates the electrolysis potential. 1 Before electrolysis; 2 after electrolysis on passing 2 F/mol; 3 conditions as with curve 2 after complete air oxidation.

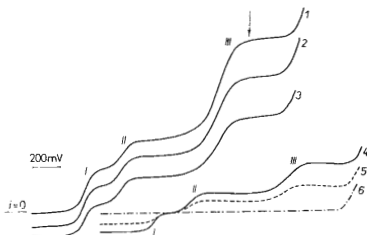


FIG. 4

Potentiostatic Electrolysis of the Nitroprusside Ion at Potentials of the Limiting Current of the Wave *III*

Phosphate buffer pH 8.8;  $10^{-3}\text{M-Na}_2\text{Fe}(\text{CN})_5\text{NO}$ ; from 0.0 V (SCE); the arrow indicates the electrolysis potential. 1 Before electrolysis; 2-6 after electrolysis on passing 2.0 F/mol; 3 1.3 F/mol; 4 2.3 F/mol; 5 3.2 F/mol; 6 4 F/mol.

than before the electrolysis (Fig. 3, curve 3). The lowering of the waves *IV* and *II'* occurs in these oxidations always in the same ratio 1 : 1. Exactly the same reoxidation pattern as just described is obtained when performing the electrolysis at potentials of the limiting current of the anodic wave *IV*. In this case during the electrolysis a turbidity appears in the solution due to dispersed metallic mercury which gradually forms a sediment.

#### *Electrolysis at Potentials of the Limiting Current of the Wave II'*

Up to the charge consumption 1 F/mol at pH 8.8 the picture is the same as with electrolysis at potentials of the limiting current of the wave *I* or *II*, viz., the anodic wave *I* is formed. A further electrolysis leads to a picture similar to that obtained when electrolyzing at potentials of the limiting current of the wave *II*, i.e. on the cathodic side the waves *II* and *III* diminish and a new wave *II'* is formed, while on the anodic side the wave *I* is decreased and the wave *IV* is formed. With further electrolysis the waves *IV* and *II'* disappear.

#### *Electrolysis at Potentials of the Limiting Current of the Wave III*

At the beginning of the electrolysis (pH 8.8) the wave *I* is shifted below the zero line of the current and the overall height of this anodic-cathodic wave is decreased (Fig. 4, curves 2 and 3). The waves *II* and *III* diminish only slightly at the beginning of the electrolysis and the decrease of the wave *III* is always larger than that of the wave *II*. In a further stage of the electrolysis when the cathodic part of the wave *I* decreases to zero also its anodic part is strongly diminished and the waves *II* and *III* decrease to a considerable extent (Fig. 4, curve 4). With further electrolysis the diminishing of all waves goes on and in the final stage only the curve corresponding to the supporting electrolyte is left on the polarogram (Fig. 4, curves 5 and 6).

#### *Influence of Excess of Free Cyanide Ions*

The hitherto described results indicate that the products of the electrolyses establish in the solution equilibria involving cyanide ions. As mentioned in the preceding paper<sup>2</sup> the addition of an excess of the cyanide ions to the nitroprusside ion solution causes a suppression of the wave *II* and enhancement of the wave *III* in such a way that their sum remains constant. This applies to higher pH values (> 8.5). At lower pH values where the wave *III* does not reach its full height<sup>2</sup> the addition of CN<sup>-</sup> ions causes a lowering of the wave *II* and an enhancement of the wave *III* but the sum of both waves is higher than before addition of the CN<sup>-</sup> ions. After electrolysis at potentials corresponding to the limiting current of the wave *I* the addition of CN<sup>-</sup> ions has a similar effect as before electrolysis, viz., suppressing of the wave *II* and enhancement of the wave *III*. In this case, however, the sum of the waves *II* and *III* is higher than before

addition of  $\text{CN}^-$  ions (after electrolysis the wave III is always lower than before electrolysis, see above) and corresponds to the threefold of the wave I of the non-reduced nitroprusside ion. On the anodic side the wave of the  $\text{CN}^-$  ions appears.

After electrolysis at potentials of the limiting current of the wave II the wave II' is not influenced by the addition of  $\text{CN}^-$  ions. When this electrolysis is carried out only partially, *i.e.* at the cathodic side the waves I, II' and III are observed, the addition of  $\text{CN}^-$  ions causes again the suppressing of the wave II and enhancement of the wave III without influencing the wave II'.

### Voltammetry

Cyclic voltammetry experiments were carried out in order to get additional information about the behaviour of the products and intermediates of the electrode processes. Three sets of experiments were performed, *viz.*, with the nitroprusside ion before electrolysis, after electrolysis on the first wave and on the second wave. In each case three different sweep regimes were applied, *viz.*, triangular fast multisweep with sweep rate 166 V/s, fast single-sweep with the same sweep rate and slow single-sweep (1.66 V/s). The sweeps were applied in potential ranges both of the individual waves and of the multiwave systems.

*The Nitroprusside Ion.* The voltammetric experiments confirmed the reversibility of the electrode process in the first and second wave and the irreversible character of the third wave. At high pH values (round 9) when sweeping in the potential region of the first wave only the reversible peaks of the first wave are observed without any trace of  $\text{CN}^-$  ions set free. At lower pH values with rapid multi-sweeps in the same potential region both anodic and cathodic small peaks of the  $\text{CN}^-$  ions are observed whilst with single sweep technique only the anodic  $\text{CN}^-$  peak appears. This result confirms that the product of the 1-electron reduction liberates  $\text{CN}^-$  ions at lower pH values.

When sweeping in the potential range of the first and second wave the peaks of the  $\text{CN}^-$  ions appear even at high pH values in a similar way as described above: with rapid multi-sweep both anodic and cathodic  $\text{CN}^-$  peaks are observed, with rapid single-sweep (starting from positive potentials) only the anodic  $\text{CN}^-$  peak appears and with slow single-sweep even the anodic  $\text{CN}^-$  peak disappears. These results show that the electrode process in the second wave is combined with liberation of  $\text{CN}^-$  ions. The disappearance of the  $\text{CN}^-$  peak observed with slow single-sweep can be explained by the recombination of the  $\text{CN}^-$  ions in the course of the anodic reoxidation of the 1-electron reduction product.

If the sweeps cover the potential range of all three waves then under the rapid multi-sweep regime again both anodic and cathodic  $\text{CN}^-$  peaks are observed (of course in addition to the reversible peak pairs corresponding to the first and second wave and the cathodic peak corresponding to the irreversible electrode process in

the third wave). In this case the  $\text{CN}^-$  peaks are distinctly larger than in the preceding case where the potential range covered only the first and second wave. With single-sweep technique only the anodic  $\text{CN}^-$  peak is observed. This shows that in the process of the third wave additional  $\text{CN}^-$  ions are liberated. A further marked difference in the rapid multi-sweep curve when going from the sweeping range covering the first two waves to that covering all three waves consists in a considerable decrease of the peak height corresponding to the first wave. This indicates that the process in the first wave is coupled with the irreversible process in the third wave from which the depolarizer cannot be returned in the rapid cycling whereas the process in the second wave under conditions of the rapid cyclization is separated from the irreversible third wave reaction and therefore the peak height corresponding to the second wave is not diminished. In single-sweep regime the diminishing of the first wave peaks is not observed which is in accordance with the above explanation.

*One-Electron Reduction Product.* Even if the one-electron electrolysis is complete, *i.e.* on the classical d.c. polarogram the first wave appears only in its anodic form, the cyclic voltammogram performed in the potential range of the first wave shows always also the cathodic peak independently whether single- or multi-sweeps are applied. This is caused by the fact that at positive potentials the reduced form is reoxidized at the electrode and this reoxidized form is then reduced cathodically at its reduction potential.

In contrast to the nitroprusside ion described in the preceding paragraph both the cathodic and anodic  $\text{CN}^-$  peaks are observed at  $\text{pH} < 8$  even with single sweeps in the potential region of the first wave. This is in accordance with the former findings that the one-electron reduction product in this pH range is substitution labile towards the  $\text{CN}^-$  ions which are spontaneously set free.

*Two-Electron Reduction Product.* When the triangular sweep starting from 0.0 V is applied to an electrolyzed solution showing in the d.c. polarography only the anodic wave IV and the cathodic wave II', a similar reoxidation is observed as described in the preceding paragraph, resulting in the appearance of the peaks corresponding to the waves I, II and III which are not present on the d.c. polarogram. This is in accordance with the fact that electrolysis at potentials of the limiting current of the anodic wave IV yields the original nitroprusside wave system (see the experimental section above). When the starting sweep potential is shifted to more negative values (*e.g.* -0.4 V) at which the d.c. polarogram shows the zero current then with the cyclic voltammetry only the cathodic peak corresponding to the wave II' is obtained.



## Absorption Spectra

In the region 200–850 nm the nitroprusside ion yields at pH 8,8 an asymmetric absorption band with the maximum at 240 nm (Fig. 5a, full curve). On electrolysis at potentials of the limiting current of the first wave this absorption band increases and at the same time anew band appears with the maximum at 345 nm (Fig. 5a, dashed curve). On standing under nitrogen both bands slightly decrease and after passing oxygen through the solution the band at 345 nm disappears completely and the band at 240 nm attains its original height (Fig. 5a, dot and dashed, and dotted curves).

On electrolysis under conditions of the 2-electron reduction (*i.e.* at potentials of the more positive part of the limiting current of the wave II) up to the consumption of 1 *F*/mol the same picture is obtained as with the electrolysis on the wave I, *viz.*, the band at 240 nm increases and the band at 345 nm appears. After surpassing 1 *F*/mol both bands diminish and a new band with the maximum at 445 nm appears (Fig. 5b, dashed curve). On standing on air the band at 445 nm decreases and the bands at 250 nm and 345 nm increase (Fig. 5b, dot and dashed curve). Passing oxygen through the solution for several minutes causes a complete disappearance of the bands at 345 nm and 445 nm and in the final stage the spectrum contains only the asymmetric band at 240 nm as with the non-reduced nitroprusside ion (Fig. 5b, dotted curve).

These results show that the products of the one- and two-electron reduction of the

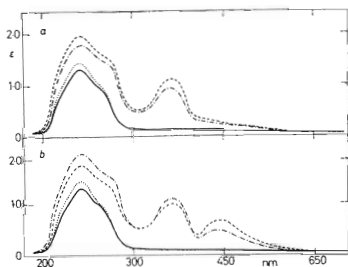


FIG. 5

## Absorption Spectra of the Nitroprusside Ion Reduction Products.

Phosphate buffer pH 8.8;  $10^{-3} \text{M-Na}_2\text{Fe}(\text{CN})_5\text{NO}$

*a*: full before electrolysis; dashed after electrolysis at potentials of the limiting current of the wave I on passing 1 *F*/mol; dot and dashed on standing for 30 min under nitrogen; dotted on passing  $\text{O}_2$  through the solution for 5 min. *b*: full before electrolysis; dashed after electrolysis at potentials of the limiting current of the wave II on passing 2 *F*/mol; dot and dashed on standing for 5 min on air; dotted as in curve 2 on passing  $\text{O}_2$  through the solution for 5 min.

nitroprusside ion can be reoxidized by oxygen to the original nitroprusside ion whereas during the reoxidation of the two-electron reduction product the one-electron reduction product is formed as an intermediate.

## DISCUSSION

The described results provide a rather detailed information about the electrochemical and chemical behaviour of the reduction products of the nitroprusside ion. The corresponding reaction scheme which can be derived from this information is shown in Fig. 6. Explanation of the symbols used are described in the text below and individual species and their reaction summarized in Tables I and II.

### One-Electron Reduction Products

The primary product of the one-electron reduction (*I*) of the nitroprusside ion (*A*) is the species  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  (*B*). This species which has in aqueous solution a greenish yellow colour (the corresponding absorption spectrum is shown in Fig. 5A, curve 2) has been described in several papers<sup>1-16</sup>. However, the conditions under which the different authors generated this species did not always warrant to obtain the proper product (*e.g.* electrolysis without potential control or without indication of the potential at which the electrolysis was performed; use of dithionite or sodium borohydride as reduction agents whereas both substances are able to reduce the nitroprusside ion by one or by two electrons — see below) and consequently some controversial results are found in the literature. *E.g.* in the paper<sup>7</sup> the authors describe a spectrum (Fig. 2, loc. cit.<sup>7</sup>) which according to our results corresponds to the product of the 2-electron reduction ( $\epsilon_{\text{max}}$  445 nm, *cf.* Fig. 5b of the present paper) and correlate the pH dependence with EPR spectra which correspond to the product

TABLE I

List of Species Contained in Fig. 6

Symbol in Fig. 6	Species	Symbol in Fig. 6	Species
A	$[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$	C <sub>2</sub>	$[\text{Fe}(\text{CN})_4(\text{NC}(\text{NO}))^{4-}$
B	$[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$	C <sub>3</sub>	?
B <sub>1</sub>	$[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$	C <sub>4</sub>	$[\text{Fe}(\text{CN})_5\text{NOH}]^{3-}$
B <sub>2</sub>	$[\text{Fe}(\text{CN})_5\text{NOH}]^{2-}$	D <sub>1</sub> = D <sub>2</sub> =	$[\text{Fe}(\text{CN})_5\text{NH}_2\text{OH}]^{3-}$
B <sub>3</sub>	$[\text{Fe}(\text{CN})_4(\text{NC})\text{NO}]^{3-}$	= D <sub>3</sub>	
C	$[\text{Fe}(\text{CN})_5\text{NO}]_4^-$	I <sub>1</sub>	$[\text{Fe}(\text{CN})_3\text{NO}]^-$
C <sub>1</sub>	$[\text{Fe}(\text{CN})_4\text{NO}]$	I <sub>2</sub>	?

of the one-electron reduction; hence follows presumably also the big discrepancy of the  $pK$  values derived from the spectroscopic and EPR results (Table I, loc. cit.<sup>7</sup>).

It is agreed that the species  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  (B) undergoes a protonation (reaction (18)) yielding the blue species  $[\text{Fe}(\text{CN})_5\text{NOH}]^{2-}$  ( $B_2$ ) even if the proton association is probably not of the normal Brønstedt type<sup>9</sup>. Although the  $pK$  values of this protonation determined by different methods have a considerable scatter<sup>7</sup> it is certain that the transition of the yellow form (B) to the blue form ( $B_2$ ) lies in slightly acidic region and the value  $pK_a = 5.8$  agrees well with the polarographic behaviour of the system<sup>1,2</sup>. Recently a suggestion was made<sup>10,16</sup> that the acid-base equilibrium instead of the reaction (18) is in fact the reaction



which would be a reaction analogous to that of the nonreduced nitroprusside ion in alkaline media (see *e.g.* papers<sup>17-19</sup> and papers cited therein). If it were so, then the "acidic" form would be  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  and the "alkaline" form  $[\text{Fe}(\text{CN})_5\text{NO}_2]^{5-}$ . This implies that the species  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  which is the primary product of the one-electron electrode reduction of the nitroprusside ion would undergo at higher pH values (*e.g.* 8-9) immediately the above mentioned hydroxylation reaction whilst in slightly acidic media it would not undergo any acid-base reaction. The polarographic behaviour of the system shows unambiguously that the reverse is true<sup>1,2</sup> so that the suggested possibility of the hydroxylation reaction instead of protonation must be rejected.

The reaction (1) is reversible and has been described in the preceding papers<sup>1,2</sup>. The reduction product  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  (B) can be easily oxidized by air oxygen in the reaction (2).

At  $\text{pH} < 8$  the system containing  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  (B) liberates free  $\text{CN}^-$  ions which are detectable both with d.c. polarography and with cyclic voltametry (see above). This indicates the existence of the reaction (3) yielding the species  $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$  ( $B_1$ ). At still lower pH values ( $< 7$ ) the dissociation of the  $\text{CN}^-$  ions continues in the reaction (4) yielding the electrochemically inactive species  $[\text{Fe}(\text{CN})_3\text{NO}]^-$  ( $I_1$ ). The existence of the series of iron-nitrosyl complexes with the mixed aquo-cyano coordination sphere between the extremes  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  and  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  was described elsewhere<sup>20</sup> and it was found that the species containing 3  $\text{CN}^-$  groups in the coordination sphere is electrochemically inactive. The reason of this inactivity is not fully clear as yet and may be associated with the delocalization of the electron density in the complex which lies at the borderline between low- and high-spin state and consequently also between  $\text{Fe}^{\text{I}}\text{-NO}^+$  and  $\text{Fe}^{\text{II}}\text{-NO}^\bullet$  configuration. For this reason it is also hard to decide if the coordination sites libe-

TABLE II

Specification of Reactions Shown in Fig. 6

Electrode reactions are denoted by double arrows:  $\langle \rightleftharpoons \rangle$  polarographically reversible,  $\rightleftharpoons$  irreversible. Chemical reactions are denoted by simple arrows:  $\longrightarrow$  one-way,  $\rightleftharpoons$  reversible reaction. The rates of the chemical reactions are divided into 4 groups: very rapid,  $t_{1/2} \ll 1$  s; rapid,  $0.1 \text{ s} < t_{1/2} < 3$  s; slow,  $t_{1/2} > 3$  s (order of several seconds); very slow,  $t_{1/2} > \text{min}$  (order of minutes to hours).

Reaction	Specification and conditions
(1) $[\text{Fe}(\text{CN})_5\text{NO}]^{2-} \langle \xrightarrow{\text{le}} \rangle [\text{Fe}(\text{CN})_5\text{NO}]^{3-}$	El. process occurring in I; $E_{1/2} = -0.365$ V at pH $> 6.5$ ; at pH $< 6.5$ $E_{1/2}$ changes due to (3) and (17); wave height pH independent <sup>2</sup> .
(2) $[\text{Fe}(\text{CN})_2\text{NO}]^{3-} \xrightarrow{\text{O}_2} [\text{Fe}(\text{CN})_5\text{NO}]^{2-}$	Rapid chem. oxidation by air oxygen
(3) $[\text{Fe}(\text{CN})_3\text{NO}]^{3-} \rightleftharpoons [\text{Fe}(\text{CN})_4\text{NO}]^{2-} + \text{CN}^-$	Rapid equil. shifted to the left at pH 9; with decreasing pH it shifts gradually to the right due to subsequent reaction $\text{CN}^- + \text{H}^+ \longrightarrow \text{HCN}$ .
(4) $[\text{Fe}(\text{CN})_4\text{NO}]^{2-} \rightleftharpoons [\text{Fe}(\text{CN})_3\text{NO}]^- + \text{CN}^-$	Rapid equil. shifted completely to the left at pH 8–9; with decreasing pH it shifts to the right (see (3)).
(5) $[\text{Fe}(\text{CN})_4\text{NO}]^{2-} \langle \xrightarrow{\text{le}} \rangle [\text{Fe}(\text{CN})_4\text{NO}]^{3-}$	El. process occurring in II at pH $> 6.5$ ; $E_{1/2} = -0.593$ V at pH $> 9.0$ ; at pH $< 9.0$ $E_{1/2}$ changes; wave height corresponds to 1-electron uptake at pH $< 6$ ; at pH $> 6$ it is decreased and attains a semikinetic character <sup>1,2</sup> .
(6) $[\text{Fe}(\text{CN})_4\text{NO}]^{3-} \xrightarrow{\text{O}_2} [\text{Fe}(\text{CN})_4\text{NO}]^{2-}$	Rapid chem. oxidation by air oxygen
(7) $[\text{Fe}(\text{CN})_5\text{NO}]^{2-} + [\text{Fe}(\text{CN})_4\text{NO}]^{3-} \rightleftharpoons [\text{Fe}(\text{CN})_4\text{NO}]^{2-} + [\text{Fe}(\text{CN})_4(\text{NC})\text{NO}]^{3-}$	Rapid chem. redox equil. shifted to the right
(8) $[\text{Fe}(\text{CN})_4(\text{NC})\text{NO}]^{3-} \rightleftharpoons [\text{Fe}(\text{CN})_4\text{NO}]^{2-} + \text{CN}^-$	Rapid equilibrium
(9) $[\text{Fe}(\text{CN})_4\text{NO}]^{3-} + \text{CN}^- \rightleftharpoons [\text{Fe}(\text{CN})_4(\text{NC})\text{NO}]^{4-}$	Slow chem. equil. shifted at pH $> 8$ to the right; with decreasing pH it shifts to the left due to $\text{CN}^- + \text{H}^+ \longrightarrow \text{HCN}$ .

Chem. reaction yielding  $\text{CN}^-$  and unidentified electroinactive products. At  $\text{pH} > 8$  the reaction is slow, with decreasing pH its rate increases.

Rapid chem. equil. shifted to the right and involving  $\text{Hg}_2^{2+}$  generated from the electrode:  $\text{Hg} - 2e \rightleftharpoons \text{Hg}_2^{2+}$  (anodic wave IV;  $E_{1/2} = 0.0 \text{ V}$ ; 2-electron at  $\text{pH} > 8$ , with decreasing pH the wave decreases parallelly to II' — see (13)).

Spontaneous disproportionation of the Hg complex under regeneration of the nitroprusside ion and metallic Hg, *r*.

El. process occurring in II';  $E_{1/2} = -1.0 \text{ V}$ ; 2-electron at  $\text{pH} > 8$ ; with decreasing pH the wave decreases being always diffusion controlled (see (9) and (10)).

El. process occurring in III at  $\text{pH} > 8$ ;  $E_{1/2} = -1.32 \text{ V}$  at pH 9.

Very rapid or rapid chem. reaction with hitherto unidentified product C<sub>3</sub>. This reaction is inserted between el. processes (14) and (17) constituting the wave III at high pH.

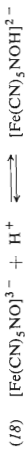
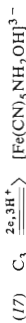
Chem. reaction yielding  $\text{CN}^-$  and unidentified electroinactive product. (I<sub>2</sub> via (10) and (16) must not be identical). At  $\text{pH} > 8$  the reaction is slow, with decreasing pH its rate increases.

El. process occurring in III at  $\text{pH} > 8$ ;  $E_{1/2}$  more positive or equal to the process of (14).

Rapid chem. equil. which manifests itself at lower pH values<sup>2</sup> ( $\text{pK} = 5.8$ ).

El. process occurring in II at  $\text{pH} < 6.5$ ;  $E_{1/2}$  is pH dependent<sup>2</sup>, wave height corresponds to 1-electron uptake at  $\text{pH} < 6$ .

El. process occurring in III at  $\text{pH} < 6.5$ ;  $E_{1/2}$  and wave height dependent on pH and supporting electrolyte<sup>1,2</sup>.



rated by the  $\text{CN}^-$  dissociation in the complexes  $\text{B}_1$  and  $\text{I}_1$  are occupied by water molecules or not (cf.  $[\text{Co}(\text{CN})_5]^{3-}$ ).

Additional elucidation of the behaviour of the species at the oxidation level B in Fig. 6 with respect to a further reduction is provided by experiments in which excess of  $\text{CN}^-$  ions was added to the system. The findings that the excess of  $\text{CN}^-$  ions added to the nitroprusside ion solution causes a suppression of the second wave without influencing the sum of the second and third wave was interpreted in the preceding paper<sup>2</sup> as a formation of  $[\text{Fe}(\text{CN})_6]^{4-}$  from  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  and thus inactivation of the complex for a further reduction in the second wave. Further it was assumed that at potentials of the third wave the nitroprusside ion is directly reduced by another route (similarly as shown in Fig. 6, reaction (14)) so that there is no time for the species  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  (B) to undergo the cyanide substitution under formation of the inactive  $[\text{Fe}(\text{CN})_6]^{4-}$ . If this mechanism were valid, then the addition of an excess of  $\text{CN}^-$  ions to the species  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  would cause its conversion to the inactive  $[\text{Fe}(\text{CN})_6]^{4-}$  resulting in the suppression of all three waves (anodic wave I, cathodic waves II and III). By experiments described above it was found, however, that under these conditions only the second wave is suppressed and the sum of the second and third wave is constant or slightly increases. Hence it follows that the depolarizer in the second wave is the species  $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$  ( $\text{B}_1$ ) and the limiting current of this wave at higher pH values ( $> 7.5$ ) is controlled by the rate of conversion of  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  (B) into  $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$  ( $\text{B}_1$ ) in the reaction (3). The addition of  $\text{CN}^-$  ions causes a shift of the equilibrium (3) to the side of B which prevents the conversion of B

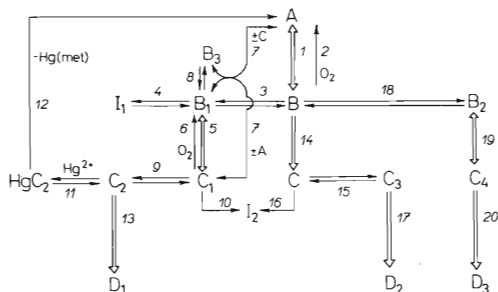


FIG. 6

#### Reaction Scheme of the Nitroprusside Ion Reduction

The symbols of the species and reactions are explained in the text and summarized in Tables I and II.

into  $B_1$  leaving the route for the process in the third wave (reactions (14)–(17)) unchanged.

The existence of the equilibrium (3) explains also small changes in the height of the second and third wave which are observed after electrolysis of the nitroprusside ion at potentials of the limiting current of the first wave. At higher pH values ( $< 7.5$ ) the second nitroprusside wave is lower than corresponds to a 1-electron uptake and has a semikinetic character<sup>1</sup>. This is caused, as mentioned above, by the chemical reaction (3) preceding the electrode reaction (5) which represents the electrode process occurring in the second wave at higher pH values. If the species  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  ( $B$ ) is present in the bulk of the solution after electrolysis it has time enough to adjust itself to the equilibrium (3) and does not escape from the electrode by diffusion which is the case when this species is generated only at the surface of the mercury dropping electrode in the polarographic reduction of the nitroprusside ion. Consequently after the 1-electron electrolysis the second wave slightly increases at higher pH values. With decreasing pH the equilibrium (3) is gradually shifted to the side of the species ( $B_1$ ) but at  $\text{pH} < 7$  the equilibrium (4) becomes operative leading to the inactive species  $[\text{Fe}(\text{CN})_3\text{NO}]^-$  ( $I_1$ ). Due to the reaction (4) the second and also the third wave is decreased after electrolysis at lower pH values and the free  $\text{CN}^-$  ions (in form of HCN) are detected in the solution. The reason why the third wave is slightly decreased after the 1-electron electrolysis (by about 7%) even at higher pH values at which the second wave is enhanced consists in the adjustment of the system  $B$ – $B_1$  to the equilibrium (3) and possibly also in some other unidentified side reaction which has, however, a minor importance for the reactivity of the system.

The following conclusions can be drawn from the above results regarding the properties of the 1-electron reduction product of the nitroprusside ion: a) The primary product is the species  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  ( $B$ ) which in acidic media undergoes a proton association leading to the species  $[\text{Fe}(\text{CN})_5\text{NOH}]^{2-}$  ( $B_2$ ). The species  $B_2$  is reduced with the uptake of 1 electron in acidic pH range and is the electroactive species in the second nitroprusside wave in this pH range. The concept of the  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-} - [\text{Fe}(\text{CN})_5\text{NO}_2]^{5-}$  reaction<sup>10,16</sup> instead of proton association is not justified. b) The species  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  is substitution labile with regard to cyanide ions and the corresponding dissociation equilibria (3) and (4) are pH dependent. The product of the first dissociation equilibrium (3) –  $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$  ( $B_1$ ) – is reduced with the uptake of 1 electron at  $\text{pH} > 7$  (the species  $B_1$  is the depolarizer in the second nitroprusside wave in this pH region rather than the ionic pair postulated in the preceding paper<sup>2</sup>). The product of the second dissociation equilibrium (4) is  $[\text{Fe}(\text{CN})_3\text{NO}]^-$  and is electro-inactive. c) The addition of the excess of  $\text{CN}^-$  ions causes a shift of the equilibrium (3) to the side of the species  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  which is the cause of the decrease of the second wave upon addition of the  $\text{CN}^-$  ions rather than the formation of the inactive complex ion  $[\text{Fe}(\text{CN})_6]^{4-}$  postulated in paper<sup>2</sup>.

## Two-Electron Reduction Products

As already mentioned, the species which is reduced in the second 1-electron wave in acidic region ( $\text{pH} < 6$ ) is the protonated form  $\text{B}_2$  and the corresponding reaction is denoted as (19) in Fig. 6 and Table II. The behaviour of the system in this pH region was described previously<sup>1,2</sup>. At higher pH values ( $> 7$ ) the species which is reduced by the uptake of 1 electron in the second wave is  $\text{B}_1$  (reaction (5)). This reaction is polarographically reversible which has been proved by experiments with the Kalousek commutator<sup>1</sup> and by cyclic voltammetry and hence it can be concluded that the primary product is  $[\text{Fe}(\text{CN})_4\text{NO}]^{3-}$  ( $\text{C}_1$ ).

However, when performing the large-area electrolysis at potentials of the second polarographic wave at higher pH values ( $< 8$ ) the anodic wave corresponding to the wave II is not observed and instead new waves III' and IV appear. From this behaviour it follows that the product  $\text{C}_1$  undergoes a chemical reaction yielding the depolarizer for the waves III' and IV. The corresponding reaction (9) is not rapid enough to be operative when using the mercury dropping electrode with the droptime round 3 s but with slow potential sweeps at the hanging-drop electrode the wave III' can be detected. This shows that the half-period amounts to several seconds so that as soon as the large-area electrolysis is completed and the system is subsequently followed polarographically the waves III' and IV are fully developed.

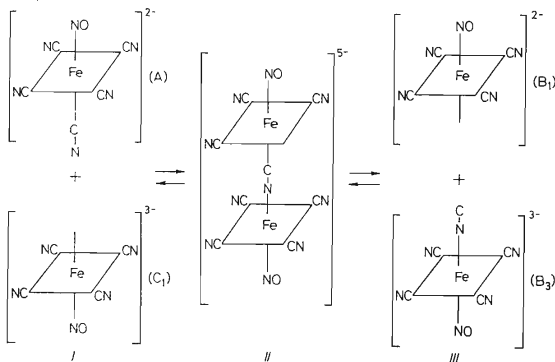


FIG. 7

Schematic Representation of the Reaction Path of the Reaction (7)



The two reversible redox systems (1) and (5) coupled together by the mobile equilibrium (3) imply the thermodynamic requirement that the oxidized form of the more positive redox couple (A) must react with the reduced form of the more negative redox couple ( $C_1$ ) under formation of species in the intermediate oxidation state (B,  $B_1$ ). That this reaction (7) which in our case can be written as  $C_1 + A \rightleftharpoons B_1 + B$  is operative is best demonstrated by the fact that in the large-area electrolysis at potentials of the second wave up to the consumption of 1 F/eq. of the nitroprusside ion (*i.e.* up to the consumption of the species A) the species  $C_1$  does not undergo the reaction (9) and the system behaves formally as if the electrolysis were performed at potentials of the first wave. Only when the species A is no more present in the solution, *i.e.* after surpassing 1 F/mol the species  $C_1$  undergoes the reaction (9) and the waves III' and IV start to develop under diminishing of the anodic wave I and the cathodic waves II and III. Chemical reduction of the nitroprusside ion by reducing agents such as  $S_2O_4^{2-}$  or  $BH_4^-$  proceeds by the same mechanism and will be described elsewhere<sup>21</sup>. Here it should be only emphasized that the extent of the reduction (1-electron or 2-electron reduction product) depends for the above reasons on the quantity of the reducing agent added.

Since one of the reactants ( $C_1$ ) in (7) has a vacant coordination site the reaction proceeds presumably by the inner-sphere mechanism shown in Fig. 7. According to this scheme the intermediate complex II having one cyanide ligand common for both iron atoms is split into the species  $B_1$  and  $B_3$ , the latter containing the N-bonded cyanide group in *trans* position to the NO group. The species  $[Fe(CN)_4(NC)NO]^{3-}$  ( $B_3$ ) has been detected<sup>11,16</sup> on the basis of EPR spectra measurements as the product of the 1-electron reduction of the nitroprusside ion by  $S_2O_4^{2-}$ . From our electrochemical results it follows that the species  $B_3$  must be in a rapid equilibrium (8) with the species B and  $B_1$  if we consider that during the course of electrolysis at potentials of the second wave no change of the half-wave potential of the waves I and II are observed whereas the depolarizer of the anodic wave I is the species B and that of the cathodic wave II is the species  $B_1$ .

The fact that the system after a complete conversion to the species  $C_2$  at high pH values does not show any presence of free  $CN^-$  ions indicates that the reaction (9) is associated with the recombination of the  $CN^-$  ions liberated in the system in (3). It is very improbable that the resulting particle is  $[Fe(CN)_5NO]^{4-}$  because in this case this species had to be reducible at more positive potentials than the species  $[Fe(CN)_4NO]^{3-}$  and this is contrary to the experimental findings (*e.g.* the easier reducibility of  $B_1$  in comparison with B). On the other hand it has been found<sup>22</sup> that the species  $[Cr(H_2O)_5CN]^{2+}$  is reduced by about 260 mV more negative than its linkage isomer  $[Cr(H_2O)_5(NC)]^{2+}$  containing the N-bonded cyanide group. By analogy with this system we conclude that the species  $C_2$  is  $[Fe(CN)_4(NC)NO]^{4-}$  which is the linkage isomer of the species C (see below).

The linkage isomerism of the cyanide ion in coordination compounds has been

recognized for some time (loc. cit.<sup>23</sup> and papers cited therein). Whereas the C-bonded cyanide ion is known as a relatively strong  $\sigma$ -donor and a weak  $\pi$ -acceptor, from the findings that the isocyano complexes are reduced at more positive potentials than the cyano complexes it follows that the N-bonded cyano group must be a weaker  $\sigma$ -donor and a stronger  $\pi$ -acceptor than the C-bonded group. When considering this property of the N-bonded cyano group then its bonding stability should increase with the decrease of the oxidation state of the central atom or other reducible parts of the complex.

According to this the stability of the isocyano complexes (or the tendency of the system to form these complexes) should increase in the sequence  $[\text{Fe}(\text{CN})_4 \cdot (\text{NC})\text{NO}]^{2-} < [\text{Fe}(\text{CN})_4(\text{NC})\text{NO}]^{3-}$  ( $\text{B}_3$ )  $< [\text{Fe}(\text{CN})_4(\text{NC})\text{NO}]^{4-}$  ( $\text{C}_2$ ) which is in accordance with our findings: no linkage isomerism is observed with the nitroprusside ion, the 1-electron reduction product forms an unstable linkage isomer ( $\text{B}_3$ ) which is in rapid equilibrium with the species  $\text{B}_1$  and  $\text{B}$ , and the 2-electron reduction product forms a stable linkage isomer  $\text{C}_2$  the dissociation equilibrium of which (9) is shifted to the side of this isomer. With decreasing pH the species  $\text{C}_1$  is inactivated by (10) yielding  $\text{CN}^-$  ions and some unidentified electroinactive products. Since this reaction cannot be reversed by increasing the pH value after electrolysis performed at lower pH value it is probable that in the reaction (10) also the NO group is split off in form of  $\text{NO}^-$  which undergoes immediately a protonation and dimerization.

The species  $\text{C}_2$  is red-coloured and exhibits an absorption band with the maximum at 445 nm (Fig. 5b, curve 2). The air oxidation returns the species  $\text{C}_2$  to the system  $\text{B}_1$ - $\text{B}$  and eventually to  $\text{A}$  (Fig. 5b, curves 3 and 4) from which it follows that the oxidation route goes over the species  $\text{C}_1$  and the reactions (6) and (2).

The anodic wave IV is due to the formation of a binuclear complex of the species  $\text{C}_2$  with mercuric ions (11) which at positive potentials are generated at the surface of the mercury electrode (when using the platinum or glassy carbon electrode the wave IV is not observed). That the mercuric rather than mercurous ions are involved follows from the 2-electron height of the wave IV combined with the most probable assumption that a 1 : 1 complex is formed. The resulting species  $\text{HgC}_2$  is, however, not stable and undergoes an internal redox process and cyanide rearrangement leading to a splitting of the binuclear complex under regeneration of the nitroprusside ion (A) and metallic mercury. This reaction (12) is observed when performing the large-area electrolysis at potentials of the limiting current of the wave IV during which metallic mercury is deposited in the bulk of the electrolyzed solution and the original nitroprusside waves are developed.

The following conclusions can be drawn regarding the properties of the 2-electron reduction products: a) The primary product  $[\text{Fe}(\text{CN})_4 \text{NO}]^{3-}$  ( $\text{C}_1$ ) is obtained at higher pH values at potentials more negative than  $-0.6$  V (s.c.e.) via the ECE mechanism  $\text{A}-\text{B}-\text{B}_1-\text{C}_1$ . b) The primary product  $\text{C}_1$  reacts with the nitroprusside

ion (A) yielding the system B-B<sub>1</sub> which corresponds to the 1-electron reduction product. *c*) At high pH values (~9) the primary product C<sub>1</sub> recombines with CN<sup>-</sup> ions under formation of the linkage isomer [Fe(CN)<sub>4</sub>(NC)NO]<sup>4-</sup> (C<sub>2</sub>). *d*) At pH < 8 the primary product C<sub>1</sub> decomposes to electrochemically inactive products I<sub>2</sub> under liberation of CN<sup>-</sup> ions. *e*) The linkage isomer C<sub>2</sub> reacts with mercuric ions under formation of a binuclear complex which decomposes regenerating the nitroprusside ion and metallic mercury. *f*) The 2-electron reduction products C<sub>1</sub>-C<sub>2</sub> are readily reoxidized by oxygen to the 1-electron reduction products and eventually to the nitroprusside ion. *g*) The linkage isomer C<sub>2</sub> is reduced electrochemically at potentials more negative than -1.0 V (s.c.e.) with the uptake of 2 electrons.

#### Four-electron Reduction Products

The four-electron reduction of the nitroprusside ion proceeds in the process corresponding to the third wave (wave III), or to the wave III'. The process occurring in the third wave in acidic media follows the reaction path A-B-B<sub>2</sub>-C<sub>4</sub>-D<sub>3</sub> in Fig. 6 and has been described previously<sup>1,2</sup>.

The wave III' represents a 2-electron reduction (13) of the species C<sub>2</sub> which itself is a 2-electron reduction product of the nitroprusside ion so that the product D<sub>1</sub> is its 4-electron reduction product. The corresponding reaction path A-B-B<sub>1</sub>-C<sub>1</sub>-C<sub>2</sub>-D<sub>1</sub> has the following features: *a*) It is fully effective only at higher pH values (>8) due to the competitive inactivation reaction (10) which operates at pH < 8. *b*) It represents energetically the easiest way of the 4-electron reduction of the nitroprusside ion (the wave III' is always more positive than the wave III). *c*) It proceeds more slowly than the other routes leading to the 4-electron reduction products which correspond to the wave III. This property is combined with the presence of the slow chemical reaction (9).

The course of the electrolysis at potentials of the limiting current of the wave III' shows that the reaction (13) proceeds without any side reactions. The product D<sub>1</sub> is an electroinactive diamagnetic species which can be destroyed in the solution by the action of mercuric ions<sup>24</sup> yielding Fe<sup>2+</sup>, CN<sup>-</sup> (bound to Hg<sup>2+</sup>) and NH<sub>2</sub>OH in the ratio 1 : 5 : 1. Hence follows the stoichiometric formula [Fe(CN)<sub>5</sub>NH<sub>2</sub>OH]<sup>3-</sup> for the product D<sub>1</sub> which has been previously postulated<sup>1,2</sup>. The product D<sub>1</sub> reacts slowly in the solution under formation of a paramagnetic species giving an EPR signal in form of a septet<sup>24</sup>. A further study of this reaction is in progress.

The reaction route A-B-C-C<sub>3</sub>-D<sub>3</sub> in Fig. 6 which is considered for elucidation of processes occurring in the wave III at higher pH values is substantiated by the following arguments which are derived from the experimental behaviour of the system: The process occurring in the wave III cannot be a continuation of the process occurring in the wave II (a further reduction of the species C<sub>1</sub>) because if the wave III is suppressed by the addition of CN<sup>-</sup> ions the wave III (measured from the limiting

current of the wave *I*) is not diminished (see experimental section). Therefore the electrode reaction (14) is considered in which the species B ( $\text{Fe}(\text{CN})_5\text{NO}^{3-}$ ) is directly reduced at potentials of the wave *III* to a species C which is presumably  $[\text{Fe}(\text{CN})_5\text{NO}]^{4-}$ . The fact that with decreasing pH the third wave decreases independently of the behaviour of the waves *I* and *II* leads to the conclusion that the species C undergoes an inactivation reaction (16) the rate of which increases with decreasing pH value of the medium. The decrease of the wave *III* with decreasing pH is accompanied by the appearance of free  $\text{CN}^-$  ions (in form of HCN) in the solution and on the contrary, addition of an excess of  $\text{CN}^-$  ions causes an enhancement of the wave *III* to its original value. Hence it follows that the reaction (16) is an equilibrium involving  $\text{CN}^-$  ions and leading to the inactive product  $\text{I}_2$  ( $\text{I}_2$  via reaction paths (10) and (16) must not be identical). The reaction (15) must be very rapid but its chemical nature cannot be specified on the basis of our experimental data and has been introduced into the scheme since the inactivation reaction has to compete with a chemical and not an electrochemical reaction the rate of which is potential dependent. The reaction (17) represents a 2-electron reaction leading to the final 4-electron reduction product  $\text{D}_2$ . This product has the same properties as described above in the case of the species  $\text{D}_1$  and hence it can be assumed that the species  $\text{D}_1$  and  $\text{D}_2$  are identical ( $[\text{Fe}(\text{CN})_5\text{NH}_2\text{OH}]^{3-}$ ).

The direct electrochemical route A-B-C... suggested as the reaction path of processes occurring in the wave *III* at higher pH values implies that at the potentials of the limiting current of this wave the species B is completely consumed by the rapid electrochemical reaction (14). Hence it follows that in the course of electrolysis at these potentials all three waves should gradually decrease in the same proportion and no anodic wave *I* should be formed. In fact, however, up to the consumption of 1 F/mol the first two waves do not decrease and are just shifted in the direction below the current zero line and only the wave *III* decreases (see experimental section and Fig. 4). Thus the system behaves as being composed of two independent systems, one being reversible and involving the waves *I* and *II* and the other one being irreversible and involving the wave *III*. A similar conclusion can be drawn from cyclic voltammetry experiments in the potential range of all three waves. This behaviour can be explained by the assumption that the species C is converted during the electrolysis into the species  $\text{C}_1$  (dissociation of one  $\text{CN}^-$  from  $[\text{Fe}(\text{CN})_5\text{NO}]^{4-}$ ) which subsequently reacts with the nitroprusside ion (A) in (7) returning partially the system to the oxidation level  $\text{B}_1$ -B. This mechanism explains the appearance of the anodic wave *I*, the seemingly independent behaviour of the wave system *I* and *II* on the one hand and of the wave *III* on the other hand during the electrolysis at potentials of the wave *III*. Also the fact that this mechanism can operate only in presence of the species A, i.e. up to the consumption of 1 F/mol, is in accordance with the experimental observation.

The conclusions regarding the 4-electron reduction of the nitroprusside ion in the region of higher pH values can be summarized in the following way. a) Depending

on the applied potential, the 4-electron reduction proceeds by two independent reaction paths, *viz.*, *via* A-B-B<sub>1</sub>-C<sub>1</sub>-C<sub>2</sub>-D<sub>1</sub> at potentials more negative than -1.0 V and *via* A-B-C-C<sub>3</sub>-D<sub>2</sub> at potentials more negative than approximately -1.3 V (s.c.e.). *b*) The final 4-electron reduction products (D<sub>1</sub> and D<sub>2</sub>) of both reaction routes show the same behaviour and presumably are identical ([Fe(CN)<sub>5</sub>NH<sub>2</sub>OH]<sup>3-</sup>). *c*) As long as the nitroprusside ions are present in the system, *i.e.* up to the consumption of 1 F/mol, in both reaction paths the intermediate 2-electron reduction product is reoxidized by the nitroprusside ion to the 1-electron reduction product.

Further aspects of the behaviour of the nitroprusside ion reduction products in connection with their chemical reactions will be published separately.

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