FORMATION OF A RADICAL INTERMEDIATE IN THE POLAROGRAPHIC REDUCTION OF 4,4'-BIPYRIDYL

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The electrochemical reduction mechanism of 4,4'-bipyridyl resembles that of 1,1'-dialkyl-4,4'-bipyridylium cations in acid and neutral media. However, the two-step reduction with the formation of a stable blue radical intermediate is complicated by the dependence of reduction on hydroxonium ion concentration and by adsorption phenomena. The radical results from the transition of a single electron into the lowest antibonding π-orbital of 4,4'-bipyridyl. Over a broad pH-region the first reduction step is reversible. In strongly alkaline solutions 4,4'-bipyridyl is reduced directly in a reversible two-electron step to the corresponding dihydro derivative. An anomalous discontinuous wave appears on the polarograms of 4,4'-bipyridyl; it is controlled by adsorption and has a faradaic character. Its origin is discussed in terms of the so-called high coverage effect and compared to the other interpretation in the literature.

One of the authors of this paper has published experimental facts[1] which revealed that the polarographic reduction of 4,4'-bipyridyl at a dropping mercury electrode occurs reversibly ($k_r > 2 . 10^{-2}$ cm s^{-1}). Other related systems were described[2] which also behaved reversibly, and the structural conditions of their reversibility were determined. The whole group of 1,1'-dialkyl-bipyridylium cations related to 4,4'-bipyridyl and 2,2'-bipyridyl was the subject of an electrochemical investigation[3-6,37]. These substances too, accept one electron reversibly (the reduction, however, occurs here without proton participation) and form intensely coloured radical cations.

Regarding the fact that the non-quaternary 4,4'-bipyridyl is the basic compound from which most of the above reversible oxidation–reduction systems are derived (in part also some redox indicators and herbicides), and in view of considerations and of attempts to apply this substance in biochemistry for preparing synthetic catalysts, it appeared important to publish more detailed experimental results for aqueous or partly aqueous solutions of 4,4'-bipyridyl and to add a more thorough discussion.

The polarographic reduction of 4,4'-bipyridyl had been first investigated by Zahlan and Linnell[7] whose results, in particular the obtained half-wave potentials, were criticized by Clark[8] as regards the accuracy of the experiments. Almost simultaneously the investigation of Falqui appeared. Neither paper[7] nor[9] is satisfactory from the present point of view both as regards the completeness of experimental facts and the numerical values and their interpretation.

EXPERIMENTAL

The samples of 4,4'-bipyridyl were of various origin (Lachema, Brno; Imperial Chemical Industries Ltd., Jealott's Hill Research Station, Bracknell, England; Professor M. T. Falqui, Cagliari, Sardinia). Both hydrochloride and the free base were investigated, but their behaviour was identical except for the anodic chloride wave. The physical constants corresponded to the data in the literature[10]. Dimethylformamide which was in some cases used in order to suppress the adsorption phenomena was a product of Merck, Darmstadt, later also of Soiuzchimexport, Soviet Union. Before measuring, the solvent had to be distilled or to be purified by chromatography on Al_2O_3 or on silicagel.

The polarographic measurements were mostly carried out with the polarograph LP 60 with an electronic pen-recorder EZ 2. (Laboratorní přístroje, Prague). The Kalousek commutator[11] had been built by the electronic workshop of this Institute. The instrument has a variable switching frequency from 25 Hz to 1·56 Hz. Polarographic curves with superimposed a.c. voltage were recorded either with a modified LP 55 polarograph (ΔE 4·5 mV) or with a Polarecord E 261 (Metrohm) in connection with the so-called a.c. Modulator. In this adaptor the value of ΔE is variable: 10, 30 and 50 mV. The dependence of instantaneous current on time for single drops was obtained with the apparatus described by Smoler[12]. The hanging mercury drop was constructed by Vogel[13]. The drop-time t_1 was in some experiments regulated by an electromagnetic tapper. Coulometric measurements were carried out with the Amel potentiostat 462, equipped with an electronic integrator of the same firm, at a stirred mercury pool electrode. In these experiments the depolarizer concentration was $1 . 10^{-3}$M and the volume to be electrolyzed 50 ml; the electrolysis cell of the same firm was applied.

RESULTS

Dependence of 4,4'-bipyridyl waves on pH. The reduction of 4,4'-bipyridyl in purely aqueous solutions takes place in several steps. As follows from Fig. 1 this substance gives in strongly acidic solutions the main wave B, somewhat increased by the immediately following reduction of hydrogen ions. At more positive potentials the distinct but very small wave A can be observed. With increasing pH-values prewave A the height of which — except for a certain increase in the region of pH 2 — does not change with the concentration of hydroxonium ions, distinctly separates from the main reduction wave B because its shift with pH to more negative potentials is at first slower than with B. Wave B slightly decreases in the region about pH 2 and retains then a constant height up to pH 4·5; it is followed by the more negative wave C, not very clearly separated from the wave corresponding to the evolution of hydrogen (in addition to this, C is deformed by the prewave C_1) and slightly higher than B. At pH 5 the height of B begins to increase and that of C to decrease; these two waves are still followed by the catalytic wave K. At pH 8·9, B and C coalesce to the double-wave D with a well-developed limiting current and a slight indication of a maximum at the beginning of the limiting current. At about pH 11 this indication in D of separation into a double wave completely disappears, as well as the small maximum and prewave A (the last curve in Fig. 1). In this region wave D has double the height of the sum $A + B$ at pH from 2·0 to 4·5. The waves B and D are diffusion-controlled. A calculation basing on the Ilkovič equation using a value for the diffusion coefficient D estimated from D of other heterocycles with a molecule of the same size[14] gave a value of n very near to 2 for wave D at pH 11; on the other hand, using $n = 2$, we obtained $D = 7 . 10^{-6}$ cm^2 s^{-1} at 20°C. This value, too, is in excellent agreement with the size of the 4,4'-bipyridyl molecule. Accordingly, the processes in acidic media, corresponding to the waves $A + B$, are one-electronic. These results were also confirmed by coulometric measurements.

The complicated course of the 4,4'-bipyridyl reduction found in aqueous solutions can be simplified by adding dimethylformamide to the solution (10% are sufficient). Here in acid media only two waves are obtained, a well-developed more positive wave and a negative one which is somewhat higher and coincides with the current corresponding to the evolution of hydrogen from the supporting electrolyte. With increasing pH the more negative wave decreases and both waves corresponding to the original waves B and C merge in single two-electron wave D. The most remarkable difference between purely aqueous solutions and those containing dimethylformamide (or some other non-aqueous solvents) lies in lowering or suppressing the discontinuous wave A.

Half-wave potentials. Fig. 2 demonstrates the half-wave potentials of waves B and D and the potential at which prewave A appears (for purely aqueous solutions). The half-wave potentials of waves C, C_1 and K are not well defined. The measured values strongly differ from the data published by Falqui[9] and only very approximately agree with the half-wave potential from the paper by Linnell and Zahlan[7]. The potential of the increase of the discontinuous wave A denoted as E_A (on purpose we do not use here the expression half-wave potential) is pH-independent up to pH 4·5; at higher pH-values dE_A/dpH equals $-0·085$ V/pH. The reduction wave B is virtually pH-independent up to pH 2, then a shift of $(E_{1/2})_B$ to more negative values occurs until pH 4; at still higher pH-values the following relation holds both for wave B and for the combined wave D: $dE_{1/2}/dpH = -0·060$ V/pH. In strongly alkaline solutions above pH 11 the half-wave potential of wave D does not depend on pH. The regions where a break can be seen on the plot E_A vs pH, and $(E_{1/2})_B$ vs pH lie in close proximity of both pK-values of 4,4'-bipyridyl as measured by Krumholz[15] from ultraviolet spectra: pK_1 4·82, pK_2 3·17. In solutions containing 20% dimethylformamide we obtained the following half-wave potentials (2 . 10^{-4}M 4,4'-bipyridyl; in volts vs S.C.E.):
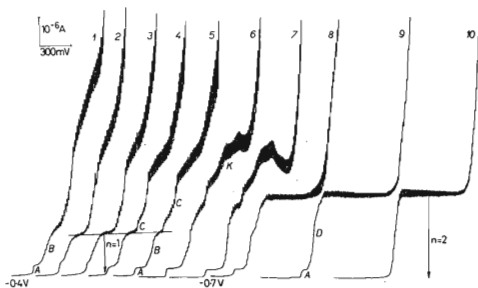

Fig. 1

Dependence of the Reduction Waves of 4,4'-Bipyridyl on pH of the Supporting Electrolyte

5 . 10^{-4}M 4,4'-Bipyridyl, Britton–Robinson buffers; curves 1 to 7 starting at $-0·40$ V vs S.C.E., curves 8 to 10 at $-0·70$ V; pH-values from left to right: 1 0·1M-H_2SO_4; 2 2·0; 3 3·5; 4 3·63; 5 4·45; 6 5·14; 7 6·35; 8 8·1; 9 8·9; 10 11·1.

pH	2·1	3·1	4·6	6·8	7·6	8·9	9·7	10·6
$(E_{1/2})_B$	−0·62	−0·67	−0·76	--	--	--	--	--
$(E_{1/2})_C$	−0·90	−0·87	−0·94	--	--	--	--	--
$(E_{1/2})_D$	--	--	--	−0·98	−1·03	−1·12	−1·15	−1·25

The slopes $dE_{1/2}/dpH$ are about −0·060 V/pH both in acidic and in alkaline media. The half-wave potentials of waves B and D are not substantially affected by adding dimethylformamide (in accordance with the influence of dimethylformamide on the reduction of other organic substances[16]).

   Concentration dependences. The plot of the height of B and D *versus* depolarizer concentration is linear in the range from $5 \cdot 10^{-5}$ to $2 \cdot 10^{-3}$M if the height of A is included. Its height, on the other hand, reaches already at low 4,4'-bipyridyl concentrations a limiting value which only slightly changes with pH. At pH 6·4 and with a dropping mercury electrode of normal characteristics this limit is attained with a $1·5 \cdot 10^{-4}$M 4,4'-bipyridyl solution; in acidic solutions this value is somewhat higher. Remarkable is the dependence of E_A and $(E_{1/2})_B$ on depolarizer concentration. For a 0·1M acetate buffer pH 4·7 E_A shifts to more positive values with increasing concentration (10^{-5}M: −0·78 V; 10^{-4}M: −0·74 V; 10^{-9}M: −0·67 V). $(E_{1/2})_B$, on the other hand, remains constant and lies at −0·85 V. In 0·1M phosphate buffer the shift proceeds in the same sense — 10^{-5}M: unmeasurable values; 10^{-4}M: −0·88 V; 10^{-3}M: −0·80 V. Here, wave B also shifts to more positive values until it finally coalesces with wave A at lower concentrations. The dependence on the height of the mercury head h, and on the drop-time t_1, on temperature and on depolarizer concentration point to the fact that wave B in acid and wave D in alkaline solutions are controlled by diffusion. Wave B has a temperature coefficient ω equal to +1·8%/°C (ω has been calculated
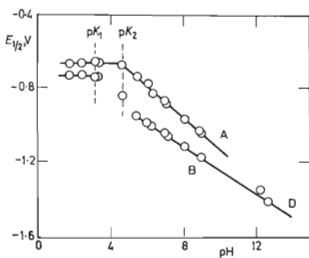
FIG. 2

Plot of Reduction Potentials of Waves A and B of $5 \cdot 10^{-4}$M 4,4'-Bipyridyl as a Function of pH of Buffered Supporting Electrolyte
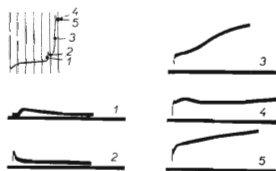
FIG. 3

Instantaneous Current–Time Curves on Single Drops (1—5) as a Function of Electrode Potential

$2 \cdot 10^{-3}$M, 4,4'-Bipyridyl; Britton–Robinson buffer pH 6·4; applied potentials: −0·92 V, −1·00 V, −1·10 V, −1·20 V, −1·30 V are shown on the polarogram in the left-hand upper corner.

from the relation $\omega = 2.3/\Delta T \log \bar{i}_2/\bar{i}_1$ at pH 6·4 over the region from 10° to 35°C. Similar values were obtained for wave D in alkaline media. The investigation of these dependences will be described in more detail in connection with the discontinuous wave A.

Logarithmic plots. The logarithmic analyses of waves B and D (*i.e.* $\log \bar{i}/(\bar{i}_d - \bar{i}) = f(E)$) give evidence of the reversibility of the corresponding electrochemical processes: at pH 2·6 the inverse slope of such a plot for wave B is 0·060 V, in strongly alkaline solutions (0·1M-NaOH) for the 2-electron wave D 0·030 V. In acid solutions the slope somewhat decreases with increasing depolarizer concentration: this is an indication of the dimerization of the primary product[17]. Because of the irreversibility of the second reduction step one cannot calculate the semiquinone formation constant from the difference $(E_{1/2})_B - (E_{1/2})_C$.

Reversibility. Since 4,4'-bipyridyl is closely related to both viologens[3-5] which in addition to their other properties are also used as redox indicators, we studied the reversibility of the electrode process in the reduction (already announced in[1]). By visual observation of a hanging mercury drop electrode with a binocular microscope or even with the naked eye the formation of an intensely blue radical could be proved. The chemical formation of this intermediate which results from the uptake of a single electron, *e.g.* in chemical reduction by mild reduction agents or in nonaqueous solvent and in absence of air under influence of sun light or ultraviolet irradiation was proved by EPR spectra[18]. Under electrochemical or polarographic conditions its formation is particularly evident at the potentials of the limiting current of wave B in acid media. The reversibility was further proved by gradual chemical reduction of the depolarizer by adding portions of $Na_2S_2O_4$ into mildly alkaline solutions; the total current, regardless if cathodic, anodic–cathodic or finally anodic, remained constant and no shifts of half-wave potentials could be observed. At higher pH values this behaviour was also found with wave D. The most important proof was given by i–t curves on single drops[19]. At the potential corresponding to the foot of wave B at pH 3 an exponent β approaching 0·20 was obtained in the log plot of the function $i = $ const. t^β. The same values resulted from measurements at the potential of the foot of the wave D in 0·1M-NaOH (at about pH 6—8 such a measurement is complicated by the close vicinity of prewave A and wave B). In good accord with the above results are also the measurements with the Kalousek commutator[11,20] when the auxiliary potential in the producing period corresponds to the limiting current of waves B or D. In both cases anodic oxidation waves are obtained, exhibiting the same half-wave potentials as the original cathodic ones. This behaviour was found with 0·1N-H_2SO_4 solutions and buffers of pH 4·1, 6·1, 8·1 and 10·0. The plot of wave-heights vs switching frequency f for which the relationship $i = $ const. $\sqrt{f}$ is valid, confirms that waves B and D are diffusion-controlled (Fig. 3).

Properties of the discontinuous prewave A. Prewave A differs in some respect (discontinuity, difference between E_A and $(E_{1/2})_B$ in certain pH-regions) from the adsorption prewaves described by Brdička[21]. For this reason both wave A alone, and its relation to waves B and D were investigated by various techniques.

The anomalous behaviour only appears at pH > pK_2 and disappears at high pH-values. The discontinuity of wave A disappears and potential E_A changes if the curve is recorded from more negative to less negative potentials. The adsorption coefficient according to Hückel is 2·3 . 10^8 (of the same order as in methylene blue), *i.e.* the maximum number of moles adsorbed on a unit area is 3·7 . 10^{-10} mol cm^{-2} and one molecule of 4,4'-bipyridyl occupies an area of 53 A^2 in adsorbed state. A model constructed by Jenšovský occupies 45 A^2 which is in good accordance with a planar adsorption of both heterocyclic nuclei and with the above polarographic measurements.

With increasing concentrations of dimethylformamide E_A shifts to more negative potentials by about 200 mV until wave A completely vanishes with 25% dimethylformamide in the solution

at pH 6·4. The height of A decreases with increasing temperature by 15% when passing from 7·5° to 48·0°C. The height of wave A (e.g. at pH 6·4 and 9·5) is a linear function of height of the mercury head and depends on controlled t_1 with an exponent at t_1 equal to $-^1/_3$. In experiments with the Kalousek commutator making use of an auxiliary potential E_{aux}, corresponding to the limiting current A, an anodic wave results with $E_{1/2}$ equal to E_A and its height is a linear function of frequency f; according to Heyrovský[22], this is characteristic of capacity and adsorption currents. With increasing concentration of 4,4'-bipyridyl the height of the commutated anodic wave A' grows only up to a limiting value and its half-wave potential is concentration-dependent. The sum of wave-heights $A' + B'$ (with E_{aux} corresponding to the limiting current of wave B) grows further under the same conditions and $(E_{1/2})_B$ is concentration-independent. In strongly alkaline solutions (pH 11·1) a clear reversibility was observed in the 2-electron wave D at $-1·23$ V when working with $E_{aux} = -1·6$ V. The ratio between the heights of waves A' and A ranges from 15 to 18 (according to pH, E, concentration), in case of B' and B this ratio varies from 2 to 3.

Polarograms with superimposed a.c. voltage according to Breyer[23] point to the fact that at pH 3·4 the oxidized form is not adsorbed, the form at the potential of the limiting current of A is strongly adsorbed and the form at the potential of the limiting current of B is also adsorbed. At pH 6·8 and 9·0 the oxidized form is strongly adsorbed and adsorption was also observed with products formed in A and B. In 0·1M-NaOH no species taking part in the reduction processes is adsorbed. The criterion of adsorption at a given potential is a comparison of the course of the curve in presence and in absence of 4,4'-bipyridyl. Electrocapillary curves ($t_1 = f(E)$) lead to the same conclusion but their poor reproducibility represents a serious drawback[24]. In classical polarography the comparison of the mean capacity currents at potentials before wave A appears[25] confirms the adsorption of 4,4'-bipyridyl e.g. at pH 6·4. The i–t curves at potentials corresponding to the limiting current of A pass through a maximum value.

By recording a current–potential curve with a stationary mercury drop electrode the reversibility of reduction in wave B was confirmed, e.g. at pH 3·4 or 6·8. Shain and Nicholson's criterion for ΔE_p of current peaks in the cathodic and anodic branch was applied here[26,27]. When polarizing from 0V up to potentials only slightly more negative than E_A ($-0·76$ V at pH 6·4) — or when remaining at E_A for, say, 15 min — a reversible anodic peak was obtained on reverse polarization. After a prolonged electrolysis at the potential of the limiting current of A we expected the
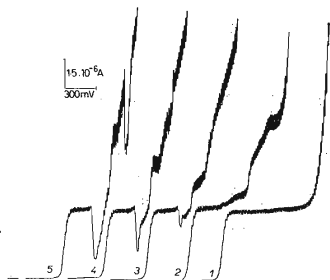

Fig. 4

Influence of 4,4'-Bipyridyl on Polarographic Reduction of Lead Ions

$5 . 10^{-4}$M-Pb(NO$_3$)$_2$ in 0·1M-HClO$_4$; conc. of 4,4'-bipyridyl: 1 0; 2 2·5 . 10^{-4}M; 3 5 . 10^{-4}M; 4 7·5 . 10^{-4}M; 5 1 . 10^{-3}M.

formation of a blue cloud around the drop and turning dark of its surface. However, the changes in close vicinity of the electrode were not so clear-cut as in wave B.

The influence of 4,4'-bipyridyl on lead reduction[28] was studied: at all pH-values the reduction of lead ions occurs at less negative potentials than that of 4,4'-bipyridyl. Regardless of the fact whether the oxidized form of 4,4'-bipyridyl is adsorbed at a given potential it does not affect the reduction of lead ions. Only at E_A a sudden suppression of the limiting current of the reduction wave of lead ions takes place; the depth of this fall depends on the ration of concentrations of both electroactive substances (Fig. 4). The current rises again only in the region of potentials that corresponds to 4,4'-bipyridyl reduction in waves B and C. Consequently, the additivity of reduction currents of lead ions and of 4,4'-bipyridyl is restored only at potentials where no intermediate from the reduction in wave A exists at the electrode. This effect which was found in 0·1M-HClO₄ and in a 0·1M acetate buffer gives evidence about the inhibitory ability of the species which is adsorbed at potentials of the limiting current of wave A on reduction of 4,4'-bipyridyl and on the reduction of other substances. In strongly alkaline solutions (in 0·1M-NaOH) the polarographic wave of lead ions is not affected, this being in accord with the fact that no form of 4,4'-bipyridyl is adsorbed here.

DISCUSSION

The course of electrochemical reduction of 4,4'-bipyridyl – in particular in acid media – resembles the mechanism of reduction of 1,1'-dialkyl-4,4'-bipyridylium cations[4−6].

The basic, very simple scheme of accepting two electrons in two steps by a particle with two positive charges in which a relatively stable, intensely blue cation radical is the intermediate, is complicated in the polarography of 4,4'-bipyridyl: the complicating factors are the existence of differently protonated species of 4,4'-bipyridyl according to pH, and, in particular, the adsorptivity of some forms participating in the electrode process.

Taking not into account the adsorption processes the electrode reactions can be described making use of conception of the π-electron septet[26] by the following equations:
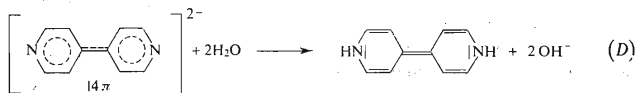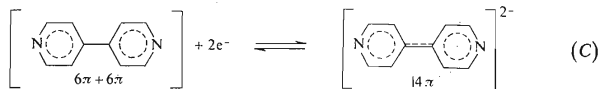

$$(A)$$
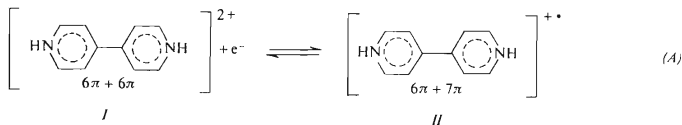
The cation radical II results thus from a transition of a single electron after protonation into the lowest antibonding π-orbital of the particle I. The formula II does not exactly describe the structure of the particle in which both pyridine nuclei are equivalent and the cation radical is symmetrical. The cation radical II is the so-called Tony's Blue described in chemical literature. In long-time electrolyses it could disappear from the electrode surface by dimer formation in a similar way as that we

found with the radical which is formed in the one-electron reduction of 1-alkyl-pyridinium cations[30]. There would be a difference only in the position of dimerization site because position 4 is blocked in case of 4,4'-bipyridyl. On polarographic curves, however, the second reduction step can be observed at more negative potentials; this leads to the dihydro derivative III:

$$\left[HN \bigcirc\!\!-\!\!\bigcirc NH \right]^{+\cdot}_{6\pi+7\pi} + e^- \longrightarrow HN \bigcirc\!\!=\!\!\bigcirc NH \qquad (B)$$

III
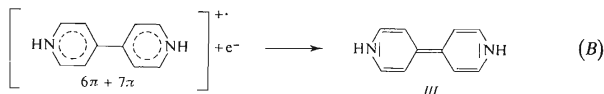
As in 1,1'-dialkyl — or 1,1'-diaryl — 4,4'-bipyridylium cations the second reduction step is polarographically irreversible; this follows particularly from the experiments with the Kalousek commutator if wave C is investigated. In addition to adsorption effects the second reduction wave may be also influenced by catalysis of the hydrogen ion reduction via the adsorbed cation radical II the properties of which could be analogous to those, found by Mairanovskii in the interpretation of pyridine waves[31]. The plot of $(E_{1/2})_B$ and $(E_{1/2})_c$ vs pH agrees with the conception of the mechanism of 4,4'-bipyridyl reduction according to Eqs (1) and (2). The potential at which wave A appears is almost pH-independent up to pH = pK_2, the half-wave potential of wave B is pH-independent up to pH = pK_1, then, between pH 3 and 5 a break appears on the $E_{1/2} = f(pH)$ — plot, and further $d(E_{1/2})_B/d$ pH is equal to -0.060 V/pH and remains constant until rather high pH-values are reached. The half-wave potential of wave D is pH-independent.

It can be concluded from the shift of half-wave potentials with pH over the whole pH-region in which only the unprotonated form of 4,4'-bipyridyl is present in the solution, that the protonation of only one nitrogen atom in the molecule is sufficient for the reduction in wave B. The plot $(E_{1/2})_C = f(pH)$ cannot be so simply depicted because the shape of the wave is distorted by adsorption effects and catalysis of hydrogen evolution. In strongly alkaline solutions $(pH > 11)$ 4,4'-bipyridyl reduction takes place in quite another manner: wave D is two-electronic, reversible according to all polarographic criteria, and both steps of the reduction cannot be separated on the polarogram:

$$\left[N \bigcirc\!\!-\!\!\bigcirc N \right]_{6\pi+6\pi} + 2e^- \rightleftharpoons \left[N \bigcirc\!\!=\!\!\bigcirc N \right]^{2-}_{14\pi} \qquad (C)$$

$$\left[N \bigcirc\!\!=\!\!\bigcirc N \right]^{2-}_{14\pi} + 2H_2O \longrightarrow HN \bigcirc\!\!=\!\!\bigcirc NH + 2OH^- \qquad (D)$$

A problem which for a longer time complicated the interpretation of the polarographic behaviour of 4,4'-bipyridyl was the prewave A.

When wave A was first observed[1] in 4,4'-bipyridyl, it was an isolated phenomenon which had no analogy in the polarographic literature. From the viewpoint of morphology a similar effect was found later by Hartley and coworkers[32] in flavine mononucleotide. This author presented a very complicated interpretation in which, in our opinion, the problem is made even more obscure although he correctly employs the conception of adsorption of the oxidized and reduced forms. Still later an intense controversion between French[33] and Russian[34,35] authors arose regarding the interpretation of prewaves and discontinuous current rises up to the limiting current in isomeric dipyridylethylenes; these substances are related to 4,4'-bipyridyl. Tedoradze[34,35] explains the prewave which he found here by the co-called high-coverage effect; in such a case the adsorbed product, covering the electrode, inhibits further reduction of the free particles diffusing towards the electrode. Laviron[33] assumes on the other hand that in the above cases of discontinuous prewaves the oxidized form is also adsorbed. Its adsorption leads to an inhibition of the reduction: the electrode is blocked by it. Only at more negative potentials the adsorbed form is reduced, and consequently a sudden desorption takes place because the reduced form is adsorbed to a lesser degree. In this moment the current increases discontinuously up to the limiting diffusion-controlled value. The prewave observed in the substances of this type is not of faradaic origin and results only from a change in the electrode capacity during the formation of the adsorbed layer or during its reorientation at a certain potential. In addition to this, both authors differ in the fact that Laviron assumes the reduction of 1,2-di(4-pyridyl) ethylene to be irreversible whereas Tedoradze considers the reduction of the analogous 2-derivative as reversible. In view of our finding the behaviour of the former to be reversible in mixtures of ethanol with water in neutral and alkaline solutions[2], Laviron's concept of reversibility should be defined in more detail even if the difference between an aqueous solution and a solution containing alcohol may be considerable.

In case of 4,4'-bipyridyl and its wave A one cannot unconditionally incline to one of the above theories if — as the case may be — the validity of only one of them is taken into account. The idea of a non-faradaic current is supported by the experimental fact that after a prolonged electrolysis at a hanging mercury drop and at the potential of wave A the blue coloration corresponding to the radical does not appear here. The i–t curves at this potential tend to have the shape described by Laviron. We also found a shift of wave A to more negative values when diluting the solution of the depolarizer. On the other hand we found that the current has a faradaic character: e.g. only the sum of wave-height A + B tends towards zero at low concentrations in wave-height vs concentration-plots, and only this sum corresponds to the consumption of one electron per molecule. Moreover, prewave A appears also in acid solutions where the oxidized form is not adsorbed; this would not be in accord with the conception of "autoinhibition". The most important finding, however, is the fact that at no pH-value a discontinuous sudden increase of current, the so-called "front-vertical", appeared, which according to Laviron should characterize the reduction of the adsorbed oxidant and a sudden desorption of the product. A similar situation arises from the suppression of the reduction wave of lead ions by adding 4,4'-bipyridyl: the suppression occurs only exactly at the potential of prewave A,

and the increase up to the current which is a sum of the reduction waves of lead ions and of 4,4'-bipyridyl is again continuous, roughly in the shape of the original wave of 4,4'-bipyridyl. Although one cannot present a final interpretation of wave A basing only on the finding of this paper we are convinced that an adsorption of both forms of the redox system plays a decisive role in the formation of wave A; this follows mainly from the a.c. polarograms.

Looking apart from the complications caused by wave A and by other adsorption effects *i.e.* when working *e.g.* with non-aqueous solvents (usually in mixture with water since protonation is desirable in this case) — and looking also apart from catalysis of hydrogen ions reduction, the polarographic reduction of 4,4'-bipyridyl is a further example of systems in which the primary reduction step of the protonated form is a particle with a π-electron septet[29], this being rather stable in our case. In contrast to simpler compounds, such as pyridine[31] and 1-alkylpyridinium cations[30], this primary act proceeds reversibly and in accordance with compounds possessing an electron-attracting substituent in position 4 of the pyridine nucleus. The 1-methyl-4-cyanopyridinium cation[36] or the viologens[5] belong to this group of substances. The reversible reduction mechanism of 4,4'-bipyridyl, however, holds only in media in which protonation is possible because in strongly alkaline solutions an also reversible, but a 2-electron mechanism according to Eq. (*3*) is operative. Our conception of a reversible redox system whose one component is 4,4'-bipyridyl — or also, 1,2-di(4-pyridyl)ethylene — has been confirmed by their recent incorporation into a synthetic catalyst[37], containing haem and 4,4'-bipyridyl and stabilized by lysine. This substance should catalyse the electron transfer onto oxygen like ferrocytochrom in nature.

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