

## ELECTROCHEMICAL AND CHEMICAL REDUCTION OF N-ALKYLPYRIDINIUM CATIONS

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Dimerisation of primary products in the electrochemical reduction of N-alkylpyridinium cations is only one among the follow-up reactions described by reactions (B) to (F). The main product of these electrochemical and chemical reactions of the primary intermediate is neither a dimer nor an alkylviologen radical but an unstable particle which can be reoxidized to the original N-alkylpyridinium cation. There is an indirect evidence that the above particle is a dihydro-pyridine. The proof of the primary N-alkylpyridinium radical by means EPR was not successful due to a high instability of this species; however, it was possible to detect a secondary alkylviologen radical by means of EPR and UV-spectra. An interaction of the primary radical with the initial depolarizer was excluded basing on experimental results.

The polarographic and electrochemical investigation of N-alkylsubstituted pyridinium cations the results of which are described in our preceding paper<sup>1</sup> confirmed the electroreduction of these compounds as an in essence one-electron process followed by dimerisation of the radical intermediate. This statement would be in accordance with the data in the literature<sup>2</sup>, but our more detailed results — based not only on classical polarography — show that the primary electrode process is, in particular with the lower homologues, followed by further chemical reactions and secondary electrochemical processes of particles thus formed.

In this paper we intend to elucidate the essence of these reactions basing on constant potential electrolyses at large-area electrodes, further to compare the results of an electrochemical reduction with those of a chemical reduction, and finally, to describe the spectral properties of the reduction products.

### EXPERIMENTAL

The *electrolytical reductions* were carried out with a three-electrode system in electrolytical cells constructed in the laboratories of this Institute<sup>3</sup>. The working cathode was represented by a mercury pool on the bottom of the cell, the auxiliary electrode was either a spiral-shaped platinum wire or a platinum foil, the reference electrode was a saturated calomel electrode. The constant potential was controlled by a potentiostat, also devised and constructed in the workshops of this Institute.

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When working in an inert atmosphere a vacuum gas seccuration method<sup>4</sup> with the corresponding instrumentation was applied. Nitrogen and argon were used as inert gases; the traces of oxygen — if present — were removed by leading the gases over a granulated BTS catalyst (Badische Anilin- und Soda-Fabrik, Ludwigshafen, Federal Republic of Germany); this procedure was followed by drying on columns containing sodium hydroxide and phosphorus pentoxide.

The EPR spectra were measured in the Institute of Macromolecular Chemistry by the courtesy of Dr J. Pilař. A JES-3B Apparatus of the firm JEOL, Tokyo, was made use of. Sealed glass capillaries, containing the radical prepared by electrolytical reduction of  $10^{-3}$ M solutions of N-alkylpyridinium iodides in 75% dimethyl sulfoxide, were used as measuring cells. The reductions were performed at  $E = -1.75$  V at a mercury pool on the bottom of the electrolysis cell bearing a teflon stopcock to which a glass capillary was connected by means of a ground glass joint (Fig. 1). By connecting this capillary to the vacuum and nitrogen line the atmospheric oxygen was removed from it by seccuration and the capillary was ready for inert filling by the electrochemically generated radical. During electrolysis the teflon stopcock was turned in such a way that a conductive connection between the mercury layer in the electrolysis cell and in the mercury reservoir was ensured. After 30 minutes of electrolysis first the mercury from the cell was removed by lowering the reservoir and then by slowly turning the stopcock the solution transferred into an evacuated capillary; later, nitrogen was let in through a glass stopcock, its pressure equilibrated *via* the nitrogen line with the atmospheric pressure and the upper part of the capillary sealed off.

Ultraviolet spectra were measured with a Unicam SP 800 spectrometer over the region from 850 to 220 nm in quartz cells adapted for work in an inert atmosphere. The radicals were prepared in the same way as for measuring the EPR spectra. From spectral cells hermetically closed with a rubber stopper held by a metal frame the atmospheric oxygen was displaced by nitrogen injected into and removed from by a syringe. The blue-coloured solutions of the radicals were transferred from the electrolytical cell by means of a syringe which had been first flushed with a stream of nitrogen. When filling the spectral cell the needle representing the nitrogen inlet was pulled out and replaced by a syringe with the blue solution of the alkylviologen radical. After the solution has been injected first the needle with the syringe must be pulled out and only after this the needle through which the nitrogen escapes from the measuring cell when the solution is added and which enables an equilibration of the pressure in the cell with that in the surrounding atmosphere.

## RESULTS

### ELECTROLYTICAL REDUCTION

In this case preparative electrolysis did not prove so successful as we expected. The reason is that the reduction potentials are rather negative and the electrochemical investigation had to be carried out at mercury electrodes. The products of the electrochemical process are strongly adsorbed on them that within 60 minutes the whole mercury layer is attacked; results in a high resistance and the electrolyses cannot be performed to completion. For this reason — in order to elucidate the follow-up reactions — we studied polarographically the changes with time of partially electrolysed  $10^{-3}$ – $10^{-2}$ M aqueous as well as mixed aqueous–non-aqueous solutions of the studied substances.

*Electrolyses of  $1 \cdot 10^{-3}$  –  $1 \cdot 10^{-2}$ M Solutions of N-Alkylpyridinium Salts in Britton–Robinson Buffers*

Purely aqueous solutions (pH 11.95) were electrolysed only for 10 minutes at  $-1.75$  V (potential of the limiting current of the cathodic wave). It follows from the difference in the wave heights of the polarographic waves before and after electrolysis (curves 1 and 2 in Fig. 2) that in all cases about 60% of the original substance were electrolysed. Curves 3–6 characterize the change with time in the partially electrolysed solution.

These changes were followed with an increased sensitivity of the polarographic recording system because unstable particles are thus characterized (electroactive products of electrolysis and of follow-up chemical reactions) the quantity of which is low in comparison to the quantity of the non-reduced starting substance and whose presence was revealed by colour changes in the solution. Immediately after electrolysis one can see a single anodic wave with  $E_{1/2} = -0.7$  V and a scarcely visible cathodic wave. The height of the anodic wave decreases with time, the height of the cathodic wave with  $E_{1/2} = -1.0$  V increases and is shifted to more negative potentials (curve 4). A second, more positive cathodic wave (curve 5) appears while the anodic wave decreases, and from the purely anodic wave an anodic-cathodic wave results with  $E_{1/2} = -0.68$  V; its anodic portion is at first much higher than the anodic one. The decrease in the height of the anodic wave becomes gradually slower and the curve attains the shape of a wave characteristic of the presence in the solution of reversible oxidation–reduction system. Later, one can observe the growth of the cathodic portion of the anodic-cathodic wave as well as a growth of the second, more negative cathodic wave whose  $E_{1/2}$  shifts to  $-1.0$  V (Fig. 6). The originally colourless

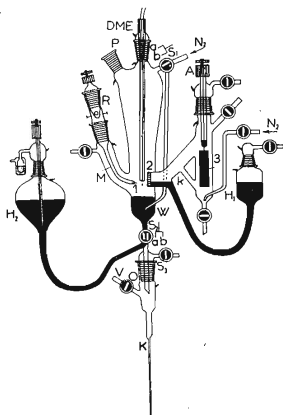
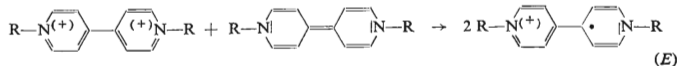
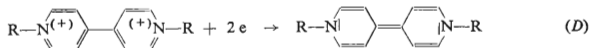
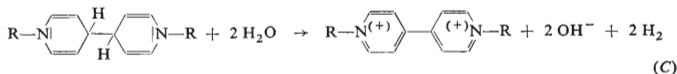
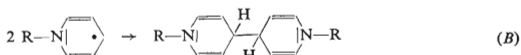


FIG. 1  
Electrolysis Cell Used for Generation of Radicals

A auxiliary electrode; R reference electrode; W mercury pool on the bottom serving as a working electrode; 3 platinum foil; K capillary; M bridge of the reference electrode; V,  $S_3$  stopcock connecting the capillary to the vacuum and nitrogen line; P free ground joint, 1 platinum wire; 2 sintered glass enabling a conducting connection between the electrolytic cell and the auxiliary electrode; k side-arm enabling a circulation of the bubbled-through electrolyte in the auxiliary electrode;  $S_1$ ,  $S_2$ ; a, b two-way stopcocks.

solutions turn slightly blue during electrolysis. This coloration becomes much more pronounced with time if the electrolysis has been interrupted: within 2 to 3 hours the solutions reach a deep blue colour. With N-ethylpyridinium iodide this process is demonstrated in Fig. 3. In this derivative both the electroreduction and the changes in the solution after interrupting the electrolysis occur in a similar way as in N-methylpyridinium iodide. The deepening in the hue of the coloration is in close connection with an increase of the anodic wave (*cf.* Fig. 3, curves 4–9) after its preceding rapid decrease (curve 3) and with an increase of the cathodic waves with  $E_{1/2} = -0.7$  V and  $E_{1/2} = -1.0$  V. If oxygen is introduced the solution suddenly decolorizes and on the polarogram one can observe two cathodic waves with  $E_{1/2} = -0.7$  V and  $E_{1/2} = -1.0$  V instead of the anodic and cathodic wave. In addition to these waves there is on all polarograms the wave of the non-electrolysed original substance which in more concentrated solutions is a double-wave with  $E_{1/2} = -1.34$  V and  $E_{1/2} = -1.48$  V for N-methylpyridinium iodide and with  $E_{1/2} = -1.31$  V and  $E_{1/2} = -1.47$  V for N-ethylpyridinium iodide. The more positive wave, appearing at first as a prewave of the cathodic reduction wave of the depolariser, increases in the course of time and finally coalesces with the more negative cathodic wave. For elucidating the reactions which take place in the solution after stopping the electrode of N-methyl and N-ethylpyridinium iodide the results of classical polarography, polarography with discontinuously changed square-wave voltage, cyclic voltammetry and coulometric measurements for N-alkylpyridinium salts have been applied. The blue coloration of the solution corresponding to the presence of the reversible oxidation–reduction system formed in the solution has been interpreted by comparing the behaviour with that of methylviologen<sup>5</sup>.

Making use of our experimental results the following electrochemical and chemical reactions must be considered:



The strong alkalisation of the solution during these processes and the formation of hydrogen bubbles both point to the fact that N,N'-dimethyltetrahydro-4,4'-bipyridine (II) formed in the dimerisation reaction gives methylviologen (III) by reaction

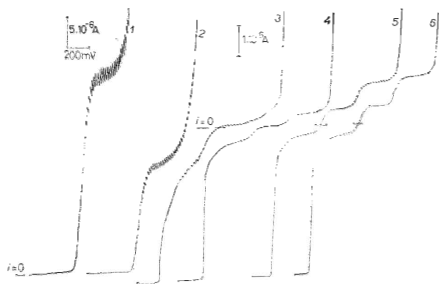


FIG. 2

Changes with Time of the Solution after Electrolysis of  $1 \cdot 10^{-2}$  M N-Methylpyridinium Iodide in 10 ml Britton-Robinson Buffer pH 11.95

Duration of electrolysis 10 minutes. 1, 2 from  $-1.0$  V, all other from  $0.0$  V. N-methylpyridinium iodide in solution 1 before electrolysis; 2 after electrolysis, 3 curve recorded immediately after electrolysis; 4–6 in 30 minutes intervals after interrupting the electrolysis.

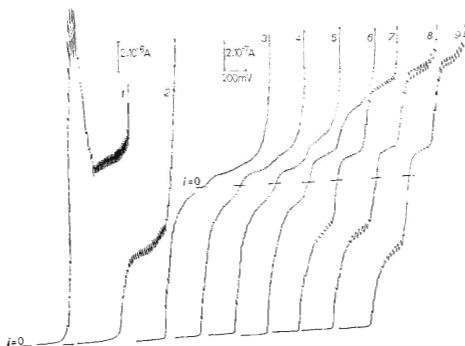


FIG. 3

Changes with Time after Electrolysis of  $1 \cdot 10^{-2}$  M N-Ethylpyridinium Iodide in 10 ml Britton-Robinson Buffer, pH 11.95

Duration of electrolysis 10 minutes, 1, 2 from  $-1.0$  V, all other curves from  $0.0$  V. 3 30 minutes after electrolysis; 4–8 in 30 minutes intervals after interrupting the electrolysis.

with water. The latter compound takes up two electrons at the potential of the electrolysis and yields (*IV*). In an oxidation–reduction reaction between *III* and *IV* the blue methylviologen radical is formed which is partly reduced during electrolysis. Basing on experiments with a Kalousek switch one can conclude that in the anodic wave on curve 3 (*cf.* Fig. 2) an oxidation of the particle *I* is seen. This unstable particle disappears from the solution within 30 minutes by follow-up reactions (*G*) and (*H*); this is why its oxidation cannot be observed on curve 3, Fig. 3 for the N-ethyl derivative.

The changes in the height and the number of waves on the polarograms confirm that even after the electrolysis has been stopped the follow-up reactions described by equations (*B*), (*C*) and (*E*) take place in the solution and produce the methylviologen radical *IV* the oxidation of which can be observed on curves 4, 5 and 6 (Fig. 3) in the anodic wave with  $E_{1/2} = -0.7$  V and their reduction in the cathodic wave with  $E_{1/2} = -1.0$  V. Although after two hours the solutions are intensely blue the height of the polarographic wave reveals that the blue radical amounts to about 5% of the original depolariser. As follows from further experiments carried out in dimethylsulfoxide the primary radical *I* is – owing to its strong reducing power –1.8 easily transformed back to the original N-alkylpyridinium cation and only a small quantity

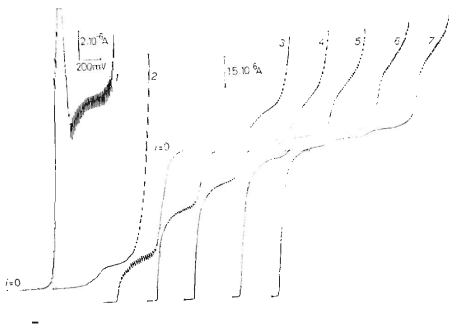


FIG. 4

Polarographic Measurement of Changes with Time in the Solution after Electrolysis of  $5 \cdot 10^{-3}$  M N-Methylpyridinium Iodide in 10 ml Britton–Robinson Buffer pH 11.95 with 50% Dimethyl Sulfoxide

Duration of electrolysis 30 minutes. 1, 2 from  $-1.0$  V, all other curves from  $0.0$  V. N-methylpyridinium iodide in solution 1 before electrolysis, 2 after electrolysis; 3–7 in 30 minutes intervals after interrupting the electrolysis.

of it is consumed in the follow-up reactions (B)–(F). The intermediate of these transitions is an unstable substance the structure of which we were not able to determine in more detail. Only basing on the half-wave potential of the reduction wave of this species ( $E_{1/2} = -1.35$  V) one can assume that it could be N-alkyl-1,4-dihydropyridine which results from a further reduction of the primary radical (G) and easily yields the N-alkylpyridinium cation (H).

The sequence of reactions for N-ethylpyridinium iodide is analogous. In electrolysis of  $1 \cdot 10^{-4}$  to  $1 \cdot 10^{-3}$  M aqueous solutions of N-n-propyl-, N-n-butyl-, N-n-pentylpyridinium iodide a voluminous yellow deposit appears. Evidently, it is a reduction intermediate whose solubility in water decreases with the growth of the length of the alkyl chain. In order to be able to follow also the changes after electrolysis with these homologues it was necessary to use solutions with 50% or 75% dimethyl sulfoxide. The presence of this solvent ensures a homogeneity of the solution during and after electrolysis.

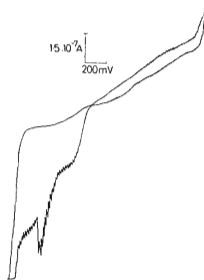


FIG. 5  
Polarographic Oxidation Waves of N,N'-Dimethyl-1,1'-dihydro-4,4'-bipyridine in Toluene-Dimethyl Sulfoxide (1 : 1) with  $N(C_3H_7)_4 \cdot ClO_4$  as Supporting Electrolyte

From +0.5 V to more negative potentials from left to right. 1 supporting electrolyte; 2 solution containing the studied substance

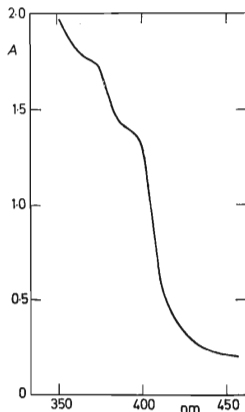


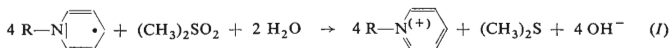
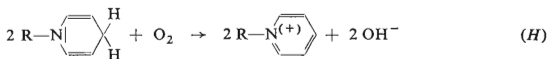
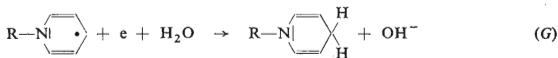
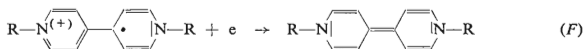
FIG. 6  
UV Spectrum of N,N'-Diethyl-1,1'-dihydro-4,4'-bipyridine in Cyclohexane

The initial concentration of N-methylpyridinium iodide before reduction was  $1 \cdot 10^{-3}$  M but only a partial electrolysis was carried out; a 1 cm cell.

*Electrolysis of N-Alkylpyridinium Cations in Partially Nonaqueous Media*

Electrolyses of N-alkylpyridinium salts were carried out in 10 ml Britton–Robinson buffers pH 11.95 containing 50% dimethyl sulfoxide. After 30 minutes of electrolysis about 70–80% of the substance were reduced, the solutions turned blue, but the intensity of the colouration is much lower than that in purely aqueous media and in the particular substances decreases with increasing length of the alkyl chain. The polarographic investigation and visual observation of the solution after the electrolysis has been stopped show that in this solution similar reactions occur as in purely aqueous solutions, but much more slowly; among other factors, this could be ascribed to an increased viscosity of the solution. A polarogram recorded immediately after electrolysis shows an anodic wave and the cathodic wave of the non-reduced depolariser. The half-wave potential of the anodic wave is shifted to more negative values with increasing the length of the alkyl chain over the region from  $-0.60$  to  $-0.78$  V. The height of this wave slowly decreases as a function of time and with all studied substances the wave is slightly shifted toward more positive potentials. The cathodic wave increases with time and a maximum appears on it which is characteristic of the studied N-alkylpyridinium cations. With an increased sensitivity of the recording instrument a small additional cathodic wave can be observed with  $E_{1/2} = -0.96$  V which increases as a function of time and with the blue colour of the solution getting more pronounced (Fig. 4). This wave, corresponding to the reduction of the alkylviologen radical<sup>5</sup>, could not be observed with the three higher homologues although it should also increase with time, in accordance with an increasing intensity of the blue coloration of the solution. This discrepancy can be interpreted by the extreme intensity of the blue coloration which enables a visual proof of the formation of the secondary radical even at concentrations where polarography is not sufficiently sensitive.

It follows from the wave-heights and from the growth of the cathodic waves of the original depolarisers that in such a solution most of the primary radical is reoxidized to the original N-alkylpyridinium cations. The disagreeable smell accompanying the electrolyses supports the assumption that the molecules of the solvent are the reduced component in the reoxidation reaction of the primary product:



The slow decrease in height of the anodic wave clearly demonstrates that the presence of an aprotic solvent stabilises the primary radical so that in this solution the referred



reactions are the electrode reduction ( $A$ ) of the original depolariser and, as a follow-up reaction the re-oxidation ( $I$ ) of the primary radical to the N-alkylpyridinium cation. This reaction can be polarographically followed as a decrease in the height of the anodic wave and an increase in that of the cathodic wave in solutions after electrolysis.

#### CHEMICAL REDUCTION OF N-ALKYLPYRIDINIUM SALTS

The chemical reduction of the N-alkylpyridinium cations with sodium amalgam in strongly alkaline solutions belongs to the oldest experiments with this type of compounds. The blue coloration that appears with an excess of amalgam was ascribed to a reduction product which could not be in that time isolated and identified<sup>6</sup> owing to its instability. In our investigations we reduced  $1 \cdot 10^{-3}$  M solutions of N-alkylpyridinium iodides with sodium amalgam. In the two lowest homologues the reduction was carried out in aqueous Britton-Robinson buffers pH 11.95, the other three derivatives were reduced in the same solution with 50% dimethyl sulfoxide. If the systems are deaerated by continuous bubbling through with nitrogen, the reduced solution attains a slightly blue coloration within several minutes. If a contact with atmospheric oxygen is perfectly prevented, the blue colour becomes deeper and in the course of 6–8 h the reduced solutions turn deeply blue.

Coloured solutions of equal intensity result after a much shorter period of time if alkylviologens are reduced with sodium amalgam or with sodium dithionite in alkaline solutions devoid of oxygen. Whereas with the sodium amalgam only a one-electron reduction takes place, giving rise to oxygen-sensitive blue alkylviologen radicals, sodium dithionite first leads to an instantaneous formation of these particles; in the course of 2–3 h they are further reduced to N,N-dialkyl-1,1'-dihydro-4,4'-bipyridines. These compounds can be extracted from the alkaline yellow-brown aqueous solutions into toluene or cyclohexane. Their solution in these solvents is red-violet and is much more sensitive towards oxygen than the blue solution of the alkylviologen radical. Even slight traces of oxygen cause a re-oxidation to the alkylviologen radical which is accompanied by a colour change from red-violet to blue. The red-violet solutions of the reduction products were subject to polarographic measurements in mixtures of toluene with dimethyl sulfoxide in a ratio 1 : 1 and with tetrapropylammonium perchlorate as supporting electrolyte.

The N,N'-dialkyl-1,1'-dihydro-4,4'-bipyridines obtained in this chemical reduction are oxidized in two anodic waves (Fig. 5). Owing to the high instability of these substances the polarograms were recorded with a speed of 100 mV/cm and consequently it was useless to carry out the log plots of the waves. The method of the slope at the half-wave potential according to von Stackelberg shows that the oxidation proceeds in two one-electron steps. The more positive anodic wave is deformed by a maximum the height of which grows with the concentration of the depolariser and with increasing length of the alkyl substituent. In such a solution the half-wave potential of the less positive wave is shifted towards more positive values with increasing alkyl substituent. For N,N'-dimethyl  $E_{1/2}$  is  $-0.76$  V for N,N'-diethyl  $-0.70$  V and for N,N'-di-n-propyl-1,1'-dihydro-4,4'-bipyridine  $E_{1/2} = -0.67$  V. The maximum on the more positive wave allows merely an assessment of its half-wave potential which in the above three cases lies in the region between  $-0.3$  and  $-0.4$  V. Since the half-wave potential is shifted to less negative potentials with longer alkyl

chains and the maximum of the more positive wave increases the shape of the double-wave becomes less clear in the higher homologues. Methylviologen is reduced in two one-electron waves with  $E_{1/2} = -0.4$  V and  $-0.8$  V. A good accordance between the half-wave potentials of anodic waves of N,N'-dimethyl-1,1'-dihydro-

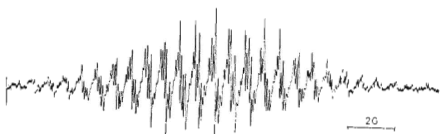


FIG. 7

EPR Spectrum of the Radical Formed After Electrolysis of N-Methylpyridinium Iodide

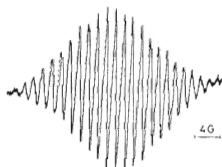


FIG. 8

EPR Spectrum of the Radical Formed After Electrolysis of N-Ethylpyridinium Iodide

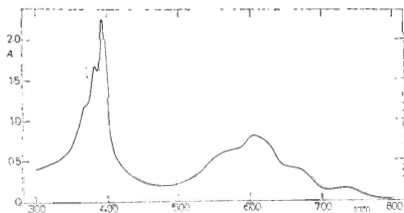


FIG. 9

UV Spectrum of Radicals Formed After Electrolysis of N-Alkylpyridinium Salts

4,4'-bipyridine and the half-wave potential of the cathodic waves of methylviologen gives evidence that we have here the oxidized and the reduced forms of the same oxidation-reduction system.

The identity of N,N'-dibutyl- and N,N'-dipentyl-1,1'-dihydro-4,4'-bipyridine was verified by their ultraviolet spectra in cyclohexane and by comparing the wave-numbers of their absorption bands with the wave-numbers given in the literature<sup>7</sup> (Fig. 6). The alkyl substituents have no perceptible effect on the position of the absorption bands and the ultraviolet spectra of these substances in cyclohexane are characterized by two shoulders at 400 nm and 375 nm.

### SPECTRAL MEASUREMENTS

Visual and electrochemical investigation of the changes in solutions after electrolysis of N-alkylpyridinium cations showed that the blue products, sensitive towards oxygen, are electroactive. The values of the half-wave potentials of the anodic and cathodic waves and the blue coloration of the solutions demonstrate that the intermediates are alkylviologen radical cations. A spectral investigation of acetonitrile and dimethyl sulfoxide solutions after electrolysis of N-alkylpyridinium cations presents further data for defining these particles in more detail.

### *Electron Paramagnetic Resonance*

The important condition for obtaining an EPR spectrum — a sufficient stability of the radicals — was ensured by delocalisation of the free unpaired electron over a long system of  $\pi$ -bonds and by a viscous solution because the radicals were generated in 75% dimethyl sulfoxide. Owing to a strong adsorption of electrolysis products at the working mercury cathode it was not possible to generate the radicals directly in a spectral cell adapted for electrolytical preparation of unstable paramagnetic particles. The small area of the mercury pool is namely contaminated by the reduction products and loses its ability to conduct electrical current. This resulted in a much more difficult way of preparing the radicals in an electrolysis cell outside the spectral cell, transferring them in an inert atmosphere and sealing them off in glass capillaries. Their lower part with a diameter of 1.0 to 1.5 mm served as the spectral cell proper (Fig. 1). The samples thus prepared were placed in the magnetic field of the spectrometer and the obtained spectra are an unambiguous proof of the existence of N-alkylviologen radicals, *i.e.* of the intermediates in the reduction in the reduction of N-alkylpyridinium cations. The best resolved spectrum was obtained with the methyl derivative (Fig. 7). It is quite identical with that obtained by us in an electrolysis of methylviologen. The spectra of the other substances investigated here are the same but in contradistinction to the N-methyl derivative they show a poor resolution (Fig. 8). To result of the interaction of the protons in the methyl group with the unpaired electron is a splitting of the absorption line into a certain number of more or less resolved components resulting thus in the hyperfine structure of the spectrum. In a radical with a longer alkyl chain there is also a weak interaction of the protons in the  $\text{CH}_2$ -groups in addition to the above interaction. The result of this fact is a still finer splitting of the absorption band. Because the spectrometer was unable to resolve this splitting we followed in these spectra only an envelope of the hyperfine structure.

By analysis of the obtained spectra the splitting constants  $a_{\text{H}}(\text{R})$  which characterize the interaction of the electron with the protons of the alkyl groups,  $a_{\text{H}}(2)$ ,  $a_{\text{H}}(3)$

for interaction with protons of different positions of the heterocyclic nucleus and the constant  $a_N$  for interaction with the heteroatom are as follows:

alkyl	$a_N$	$a_H(R)$	$a_H(2)$	$a_H(3)$
R = CH <sub>3</sub>	4.30	4.14	1.62	1.34
R > CH <sub>3</sub>	4.20	4.20	1.40	1.40

(R > CH<sub>3</sub> is: C<sub>2</sub>H<sub>5</sub>, n-C<sub>3</sub>H<sub>7</sub>, n-C<sub>4</sub>H<sub>9</sub>, n-C<sub>5</sub>H<sub>11</sub>).

The accuracy of the above constants the value of which depends on the probability of the occurrence of the unpaired electron in close vicinity of the nucleus of the corresponding atom has been verified by simulated spectra taking into account a Lorentzian shape of the spectral line. The constants are also in good accordance with the constants obtained for 4,4'-bipyridine and methylviologen radical in 95% ethanol<sup>8</sup>.

### Ultraviolet Spectra

The ultraviolet spectra of the alkylviologen radicals are virtually identical for all five derivatives. Over a region from 220 nm to 850 nm one can follow several absorption bands (Fig. 9) the position of which is not affected by the alkyl group on the nitrogen atom. A theoretical calculation of the spectrum of the methylviologen radical was carried out by the SCF method for open-shell systems<sup>9</sup>: the calculated and experimental positions of the bands were compared. The good accordance is a proof that the obtained spectrum corresponds to an alkylviologen radical.

### DISCUSSION

The conception of a simple fundamental reduction mechanism is complicated by the results of coulometric measurements and of electrolyses. They demonstrate that the dimerisation of the primary products is only one of the follow-up reactions occurring in the bulk of the solution, giving thus rise to further electroactive substances. The values of  $n_{ap}$  obtained from coulometric measurements with a stirred mercury pool electrode<sup>1</sup> considerably exceed the value of 1 and show what an important role — in particular in the methyl and ethyl derivative — is played by the reactions of the primary product, described by equations (B)–(F); in addition to this the further reduction to dihydropyridine (G) and a re-oxidation of the latter to the original N-alkylpyridinium cation according to (H) must not be forgotten. A note is necessary: it is difficult to decide whether all radicals formed in the primary reduction step dimerise (B) or whether only a part of them dimerises and the remaining particles are immediately further reduced according to Eq. (G). It follows from our experimental findings that in purely aqueous solutions the main product of the follow-up

chemical and electrochemical reactions is neither the dimer nor the alkyviologen radical but an unstable particle which is re-oxidized to the original depolariser.

Basing only on the instability in the solution and on its re-oxidation to the N-alkylpyridinium cation one could assume that the above particle is a dihydropyridine. Unsubstituted N-alkyldihydropyridines are compounds about which there are only few data to be found in the literature; most papers<sup>10</sup> confirm their instability and oxidizability by atmospheric oxygen or silver nitrate to quaternary pyridinium cations.

It has been shown that the formation of dihydropyridine occurs *via* the above-mentioned radical, *i.e.* a particle with a  $\pi$ -electron septet. The results of the semi-empirical LCAO MO-method, used for the investigation of reactivity<sup>11</sup> lead to the assumption that by further reduction of N-alkylpyridinium radical prevalently N-alkyl-1,4-dihydropyridine will be formed. However, it is very difficult to choose such reaction conditions that solely either 1,2-dihydro- or 1,4-dihydropyridine results. This specific reduction which was successful only in several cases<sup>12</sup> is still made more difficult by the easy oxidizability or polymer formation of the reduction intermediates.

The application of the EPR spectroscopy for detecting the primary N-alkylpyridinium radicals was not successful because of their high instability. The delocalisation of the unpaired electron over the electron system of the pyridine nucleus does not increase the stability of the N-alkylpyridinium ring to such an extent that the concentration of the radicals in the sample does not change with time. For this reason the particles immediately react according to (B)-(F); the key-intermediate is the alkyviologen radical so that instead of the EPR spectrum of the primary radical the spectrum of the product of its follow-up reaction was obtained; accordingly this product can be denoted as the secondary radical. Although the concentration of the secondary radical in the reduced solution is not higher than 10% of the original concentration of the N-alkylpyridinium cation the high stability of its  $\pi$ -electron system enabled a spectral proof of this particle. In addition to the EPR spectra the secondary radical is also characterised by its ultraviolet spectrum in acetonitrile or that of the product of its further reduction in toluene. The alkyviologen radicals can be namely chemically reduced to N,N'-dialkyl-1,1'-dihydro-4,4'-bipyridines.

An interaction with the original depolariser could be taken into account as a possible follow-up reaction of the primary product. The course of this reaction in the solution after reduction should result in a decrease in height of the cathodic wave of the original depolariser with time if the electrolysis is interrupted. The experiments, however, point to just an opposite phenomenon. Basing on chemical reaction mechanism this reaction would yield a N,N'-dialkyl-2,4'-bipyridinium radical cation or a N,N'-dialkyl-2,2'-bipyridinium radical cation. An existence of these two types of particles in the solution would necessarily affect the EPR spectra. Both the shape and an analysis of the obtained spectra exclude the existence of these species in the solution. Owing to a lack of experimental proofs the reaction between the original depolariser and the primary radical was not considered.

Here is a tendency in every primary radical to form — in one or several follow-up reactions — a new substance which is the most stable under given reaction conditions. It follows from our experimental results that this species is the alkylviologen radical. Although it contains an unpaired electron it is very stable and can be kept in a sealed glass ampoule under nitrogen atmosphere for several months in an unchanged state.

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