REACTIONS OF CYCLAMMONIUM CATIONS

XXII.* THE INFLUENCE OF SUBSTITUENTS ON THE HETEROATOM ON THE EASE OF POLAROGRAPHIC REDUCTION OF PYRIDINIUM CATIONS

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The polarographic reduction of pyridinium cations with various substituents both in the nucleus and at the heteroatom has been investigated. The reduction mechanism is determined by the substituents in the pyridine nucleus. Substituents attached to the nitrogen atom and to carbon atoms of the ring affect the electrophilicity of pyridinium cations differently.

As is well known, in the polarographic reduction of pyridinium cations the transfer of one electron into the lowest vacant π orbital of the pyridinium nucleus takes place with the formation of stable heteroaromatic systems with seven π electrons (π septet) [2, 3] which have been isolated in some cases [4]. The one-electron reduction of pyridinium salts may be considered as the simplest case of nucleophilic substitution, since in the majority of cases such reactions also include an intermediate stage of one-electron transfer with the formation of π complexes (or charge-transfer complexes). In view of this, the values of the half-wave potentials of the reduction of pyridinium cations may be considered as a measure of their electrophilicity and, consequently, their activity in reactions with nucleophiles.

We have investigated the polarographic reduction of pyridinium salts with various substituents in the ring and on the heteroatom in order to determine their influence on the electrophilicity of the cations. It is known that the quaternary nitrogen atom in an azomethine $\rangle\overset{+}{N}{=}CH{-}$ is not an obstacle to the transfer of the conjugation effects of substituents [5]. There is also information on the possibility of the transfer of electronic effects of substituents attached to the nitrogen heteroatom in quaternary pyridinium salts [6-8]. At the same time, measurement of the rates of the deuterium-exchange reactions of pyridinium salts with various N substituents has shown that in the main only the induction effects of the substituents are transmitted through $\rangle\overset{+}{N}{=}$ [9]. Our observations of the retention of the nucleophilic activity of an NH_2 group attached to the nitrogen atom of a pyridinium cation also indicates a weak $p-\pi$ conjugation or the absence of conjugation of the p electrons of the exocyclic nitrogen atom with the ring (in contrast to an α- or a γ-amino group where the existence of conjugation causes a displacement of the p electrons of the amino group and the weakening of its nucleophilic activity) [10].

To determine the nature of the electronic transmission capability of a ring nitrogen atom bearing a positive charge, we have investigated the polarographic behavior of three groups of pyridinium salts (I-III).

In contrast to the salts (I), in the quaternary salts (II and III) conjugation of R with the nucleus is impossible because of the acoplanarity of the molecule [11]. Consequently, by comparing the influence of the substituent R on the value of the half-wave potential of all three groups of salts it is possible to deter-

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*For Communication XXI, see [1].

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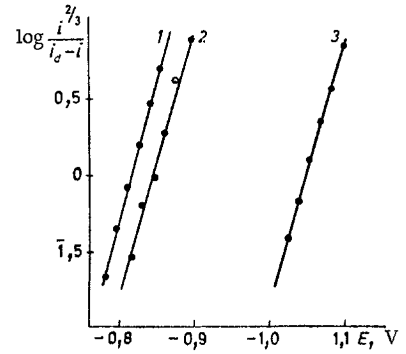


Fig. 1. Dependence of log $[i^{2/3}/(i_d - i)]$ on E in the reduction of the salts (I) in DMFA: 1) (Ia); 2) (Ib); 3) (Ie).

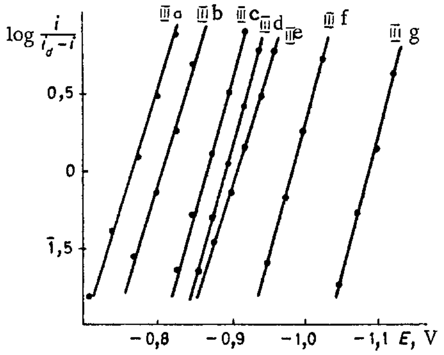


Fig. 2. Dependence of log $[i/(i_d - i)]$ on E in the reduction of the salts (III) in DMFA.

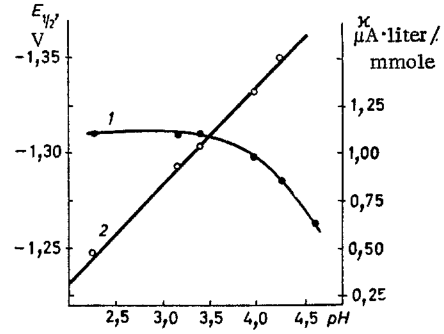
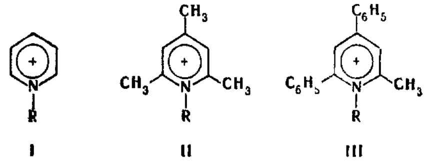


Fig. 3. Dependence of the proportionality coefficient of the Ilkovic equation $\varkappa = 1/c$ (1) and of $E_{1/2}$ on the pH of the solution (2) in the reduction of (IIIg) in 50% DMFA.

mine the contribution of the M effect to the total influence of N substituents in the salts (I) on the change in the electrophilicity of these cations.



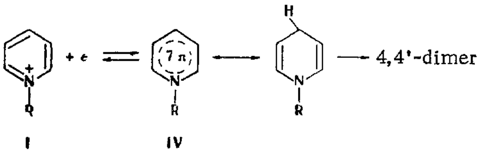
I II III

R = CH_3, H, C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4, p-BrC_6H_4

The polarographic study of the salts was performed in DMFA on a support of 0.05 M $KClO_4$, and also in aqueous dimethylformamide media at various pH values. In DMFA, the cations (I) are reduced in one stage. In agreement with the Ilkovic equation, within wide limits the current is proportional to the concentration of depolarizer. The diffusion coefficient of N-methylpyridine calculated from this equation proved to be $1.1 \cdot 10^{-5}$ cm^2 · sec^{-1}. Just the same value of D for aqueous solutions at 25°C has been obtained from the values of the mobility of N-methylpyridine at infinite dilution [12].

Since the viscosities of water and DMFA at 25°C are practically identical, it may be assumed that in DMFA the nature of the reduction will not change, i.e., these compounds are reduced with the consumption of one electron. According to theory [2], the subsequent fast dimerization reaction will determine the shape of the wave and the dependence of $E_{1/2}$ on the concentration of depolarizer: $E_{1/2}$ shifts to positive potentials with a rise in the concentration of depolarizer, and the wave is rectified in a plot of log $[i^{2/3}/(i_d - i)]$ versus E (Fig. 1), the characteristic potential (ε_0) being independent of the concentration and the reciprocal of the slope being close to the theoretical value of 59 mV (Table 1).

The reversible nature of the wave is confirmed by the results of cyclic oscillopolarography, the anodic peak of the oxidation of the radicals obtained with cathodic sweeping of the potential being capable of observation only at a sweep velocity of 1 V/sec. This is apparently due to the rapid dimerization of the radicals (IV), as a result of which they disappear from the sphere of the reaction. Thus, the reduction of the compounds of series (I) can be represented by the scheme below. The dimerization of the radicals predominantly at position 4 agrees with a quantum-chemical calculation of electron density.



(1)

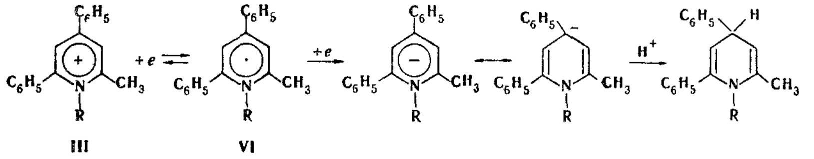
In aqueous dimethylformamide solutions the reduction of the compounds of series (I) is complicated to a considerable degree by a whole combination of adsorption phenomena connected with the adsorption both of the depolarizer and of the dimeric reaction products. In addition to this, the dimeric products possess a catalytic activity, and for compounds with R = Ph or C_6H_4X, they are capable of being reduced at more negative potentials.

TABLE 1. Parameters of the Polarographic Waves of the Reduction of Substituted Pyridinium Salts in Anhydrous DMFA on a Support of 0.05 M $KClO_4$

Comp.	R	$-\varepsilon_{0}$, V	$\frac{nF}{RT}$, mV	Comp.	R	$-E_{1/2}$, V	$\frac{nF}{RT}$, mV	Comp.	R	$-E^{1}_{1/2}$, V	$\frac{nF}{RT}$, mV	$-E^{2}_{1/2}$, V
Ia	C_6H_5	0,815	58	IIa	$4\text{-}BrC_6H_4$	1,390	50	IIIa	$4\text{-}BrC_6H_4$	0,780	62	1,225
Ib	$4\text{-}CH_3C_6H_4$	0,845	52	IIb	$4\text{-}CH_3C_6H_4$	1,405	45	IIIb	$4\text{-}ClC_6H_4$	0,820	62	1,275
Ic	$1\text{-}C_{10}H_7$	0,845	62	IIc	CH_3	1,495	48	IIIc	$4\text{-}CH_3C_6H_4$	0,870	57	1,380
Id	$4\text{-}CH_3OC_6H_4$	0,850	55					IIId	C_6H_5	0,890	58	1,475
Ie	CH_3	1,050	56					IIIe	$4\text{-}CH_3OC_6H_4$	0,910	64	1,560
								IIIf	CH_3	0,985	58	1,570
								IIIg	H	0,990	55	—

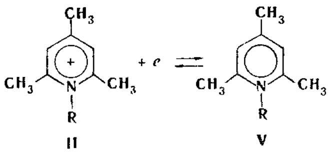
In contrast to series (I), the compounds of series (III) are reduced in two stages in DMFA. For this series, in the first stage, again, the transfer of one electron takes place with the formation of a radical, but in this case dimerization at the γ or the α position of the pyridine ring is hindered. In agreement with this, the shape of the wave now obeys the equation for an electrode process with a reversible electrochemical stage (Fig. 2), the reciprocal of the slope of the wave in semilogarithmic coordinates being close to the theoretical value of 59 mV (Table 1), and the anodic peak of the oxidation of the radicals being recorded on cyclic oscillopolarograms.

On passing to aqueous dimethylformamide solutions, only the nature of the first wave changes, which is apparently also due to the appearance of adsorption phenomena at the dropping mercury electrode. The second wave is observed at more negative potentials, and therefore the adsorption of the depolarizer and of the reaction products has practically no effect on this stage of reduction. The $E_{1/2}$ value of the second wave does not depend either on the concentration of the water or on the pH of the solution, and the height of this wave also corresponds to the transfer of one electron. Thus, at sufficiently negative potentials the activity of the electrons is so high that the reduction of the radicals takes place faster than their reaction with the solvent, and protonation takes place only after the transfer of a second electron.



(2)

It is interesting to note that the compounds of series (II) for which dimerization after the transfer of an electron is also difficult are reduced in only one stage (Table 1).



(3)

This is apparently due to the fact that in the radical (VI), due to conjugation with two phenyl substituents in the pyridine ring, delocalization of the electron is considerably greater than in the radical (V), as a result of which (VI) acquires electrophilic properties and is capable of taking up one more electron, after which the protonation stage follows with the formation of an N derivative of 1,4-dihydropyridine (scheme 2).

Among the compounds of series (III), a special place is occupied by 2-methyl-4,6-diphenylpyridinium (IIIg, R = H). As is well known, pyridine catalyzes the discharge of hydrogen from aqueous solutions [13]. One of the stages of the formation of the catalytic hydrogen wave is the bimolecular reaction of the radicals obtained as a result of the transfer of an electron to the protonated form of the catalyst. As a result of this reaction the regeneration of the main form of the catalyst and the liberation of a molecule of hydrogen take place. The hindrance to the dimerization reaction in the case of (VI) must lead to a disturbance in the classical scheme of hydrogen evolution. In DMFA the one-stage reduction of (IIIg) is observed, the height of the wave corresponding to the transfer of one electron and being determined by the diffusion of (IIIg). This wave may be connected with the transfer of an electron either to the cation of (IIIg) or to a solvated proton formed in the electrode space on the dissociation of this cation. In both cases, in an alkaline medium when pH ≫ pK, (IIIg) should not show polarographic activity. In actual fact, in aqueous dimethylformamide solutions at $pH > 8$ (IIIg) is not reduced up to the potentials of the discharge of the ion, while at $pH < 3$ a wave is observed which is proportional to the concentration of (IIIg) in agreement with the Ilkovic equation. At $pH > 3$, the height of the wave decreases, acquiring a kinetic nature, which corresponds to the deprotonation of the cation (IIIg). In the pH 2-4.6 region, $E_{1/2}$ shifts linearly to negative potentials, and $\Delta E_{1/2}/\Delta pH$ is 52 mV, which is close to the theoretical value of 59 mV for an electron process in which the number of electrons participating in the reaction is equal to the number of protons (Fig. 3). Thus, (IIIg) is a catalyst only in the sense that the transfer of an electron to this cation takes place more readily than to a hydrogen ion, while the height of the wave is determined not by the rate of reaction of the basic form of (IIIg) with proton donors but by the diffusion of (IIIg) to the electrode. According to the results of cyclic oscillopolarography, the wave of (IIIg) both in DMFA and in aqueous dimethylformamide media is reversible. The subsequent fate of the radical of (IIIg) is unknown, and it can be stated only that it is unstable and disproportionates fairly rapidly in solution. In actual fact, the anodic process of its oxidation can be recorded only at very high rates of sweep of the potential. The absence of a second wave on the polarograms of (IIIg) can probably be connected with the same thing (Table 1).

The dimerization of the radical of (V) must also be hindered. In addition to this, the steepness of the wave, which is greater than the theoretical value for reversible one-electron reduction, shows the bimolecularity of the chemical stage taking place after the transfer of an electron.

As can be seen from Table 1, in actual fact the substituents on the heteroatom have a fundamental influence on the half-wave potential and ε_0: electron-accepting substituents facilitate reduction in all cases, and electron-donating substituents oppose it. It has been found that the values of ε_0 for the salts (I) correlate satisfactorily with Taft's σ^0 constants, which may indicate the presence of some conjugation of the substituents with the nucleus; in the case of the salts (II, III) no such correlation was observed.

According to the literature [8], the values of $E_{1/2}$ of the salts of series (I) correlate with Hammett's σ constants, with $\rho = 0.3$ V and $E_{1/2}$ of N-phenylpyridinium being -1.02 V. Unfortunately, in the paper cited there is no information on the medium in which the measurements were performed, and also why the values of $E_{1/2}$, which in this case depend on the concentration of the depolarizer, and not the values of the characteristic potential ε_0 [2], were used for correlation.

On comparing the values of $E_{1/2}$ for the reduction of the salts (I, II, and III) with identical substituents on the heteroatom it can be seen that the salts (I) are reduced most easily, and then (II) and (III). This shows a reduction in the electrophilicity of the pyridinium cations with the introduction into the nucleus of alkyl groups (+I effect) and of phenyl substituents (−I, +M effect). It is known that the phenyl group possesses weak electron-accepting properties under the action of an inductive effect and can both attract and repel electrons under the action of the conjugation effect. As a substituent in the pyridine ring, a 4-phenyl group is a donor, while a phenyl group in position 2 is a weak acceptor [14]. Our results also indicate the electron-donating nature of a 4-phenyl group conjugated with the pyridine nucleus. However, the phenyl substituent attached to the heteroatom caused a lowering of the reduction potential in all cases, which indicates its electron-accepting action. The very slight electron-donating effect of a p-methoxyphenyl substituent (as compared with phenyl) and the weak electron-accepting effect of p-BrC_6H_4 and p-ClC_6H_4 groups permits us to conclude that the action of substituents on the heteroatom is not limited to their inductive effect. There is also a partial conjugation of the rings; however, the inductive effect undoubtedly plays an immeasurably greater part. It must be mentioned that in relation to the tropylium cation, of which the pyridinium cation is a heteroanalog, the phenyl group likewise behaves as a weak electron-accepting substituent [15].

The electrophilic nature of pyridinyl radicals that we have established permits an explanation of many experimental facts on the free-radical hetarylation of organic compounds, in which pyridinyl radicals, as a rule, attack the position with the highest π-electron density. As can be seen from Table 1, the potentials of the second one-electron wave of the reduction of the radical (VI) also increase uniformly with a rise in the electron-accepting properties of the substituents on the nitrogen, which agrees with our hypothesis of the common nature of the mechanism of these two processes.

EXPERIMENTAL

The polarographic investigations were performed in a thermostated cell at 25 ± 0.1°C. The polarograms were recorded with a PO-4 Radiometer (Denmark) polarograph. In this case, a dropping mercury electrode with forced detachment of the drops with the aid of a blade ($m = 0.73$ mg/sec, $t = 0.3$ sec) was used as the working electrode. The oscillopolarographic investigation was performed on a 02TsLA oscillographic polarograph with a device for working under "first drop" conditions. The dropping mercury electrode had the characteristics m = 0.92 mg/sec, t = 6.8 sec. On working in aqueous DMFA media a saturated calomel electrode was used as the anode, and in DMFA a silver wire immersed in the solution undergoing polarography. The quaternary pyridinium salts were obtained by published methods [16-19]; their constants corresponded to those given in the literature.

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