

POLAROGRAPHIC REDUCTION OF 1-(*p*-SUBSTITUTED BENZYL)-  
-3-CYANOPYRIDINIUM CHLORIDES

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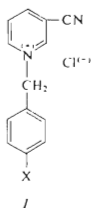
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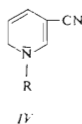
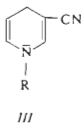
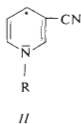
Received October 8th, 1981

Reduction of 3-cyanopyridinium salts has been studied on the mercury dropping electrode. Solvent and substituent effects and pH of the medium have been shown to modify in a certain extent differently the polarographic characteristics as compared with analogous 3-carbamoyl derivatives, which is due to higher electronegativity of the studied cations.

In the context of studies of electrochemical behaviour of  $\text{NAD}^+$  models our previous communication<sup>1</sup> dealt with substituent effects in a series of *para*-substituted 1-benzyl-3-cyanopyridinium salts. Correlation of half-wave potentials of these depolarizers with the Hammett  $\sigma_p$  constants showed also that the solvent used affects strongly decomposition of the correlation field, which is probably due to changed mechanism of the polarographic process. With the aim of verification of general character



- Ia: X = OCH<sub>3</sub>
- Ib: X = CH<sub>3</sub>
- Ic: X = H
- Id: X = F
- Ie: X = Cl
- If: X = COOCH<sub>3</sub>
- Ig: X = CN
- Ih: X = NO<sub>2</sub>
- Ii: X = N(CH<sub>3</sub>)<sub>2</sub>



of this finding we decided to investigate another analogous set of  $\text{NAD}^+$  models,

namely the *para*-substituted 1-benzyl-3-cyanopyridinium chlorides *Ia-i*, which differs from the above-mentioned set by impossibility of deprotonation and higher electron-acceptor effect of the functional group at 3 position.

Out of the quaternary salts of 3-cyanopyridine 1-methyl-3-cyanopyridinium iodide was only studied electrochemically<sup>2,3</sup>. Polarographic reduction of aqueous solutions of this salt was found to proceed in two waves<sup>3</sup>, the first wave (A) corresponding to formation of readily dimerizing radical *II* (R = CH<sub>3</sub>) and the second wave (B) corresponding to subsequent reduction down to the respective 1,4- or 1,6-dihydropyridine derivative (*III* or *IV*, respectively, R = CH<sub>3</sub>). Hence this course is analogous to that of 3-amidic NAD<sup>+</sup> models<sup>4-6</sup> and 3-cyanopyridine itself<sup>7-9</sup>, whereas electroreduction of 2- and 4-cyanopyridinium derivatives concerns the cyano groups<sup>6,10-12</sup>.

This paper brings results of studies of polarographic reductions on dropping mercury electrode for the depolarizers *Ia-h*, since our attempts at preparation of the dimethylamino derivative *Ii* have been unsuccessful so far. Attention is focused mainly on solvent and substituent effects effects of the investigated process.

## EXPERIMENTAL

The temperature data are not corrected. The melting points were measured on a Boetius apparatus (GDR). The UV spectra were measured with a Spekord UV-VIS apparatus (GDR), the <sup>1</sup>H NMR spectra were measured with a Varian 100 XL apparatus. The spectra and elemental analyses were carried out in Central Laboratory of our Institute.

### Syntheses of the Used Substances

3-Cyanopyridine was prepared by dehydration of nicotinamide with phosphorus pentoxide<sup>13</sup>. The quaternary salts *Ic* and *Ie* were prepared by reaction of 3-cyanopyridine with the corresponding benzyl chlorides. Their structure was verified by elemental analysis, <sup>1</sup>H NMR spectra and melting points: *Ic* 204–206°C, dec. (ref.<sup>14</sup> m.p. 207–209°C); *Ie* 198–199°C, dec. (ref.<sup>15</sup> m.p. 200–202°C). The other compounds *Ia*, *Ib*, *Id*, *If-h* were prepared by 2–3 days heating of the starting components in anhydrous solvents to boiling or with higher boiling solvents at 100°C. The product was obtained by crystallization from the reaction mixture and subsequent recrystallization from aqueous methanol or ethanol. The experimental and <sup>1</sup>H NMR spectral data are given in Table I.

The compound *Ii* could not be prepared, because the required 1-(2,4-dinitrophenyl)-3-cyanopyridinium chloride was not formed in any of the procedures used. 3-Cyanopyridine and 2,4-dinitrochlorobenzene either do not react at all (in toluene) or give decomposition products (in DMSO or in melt). Heating in anhydrous DMF only gave dimethylformamide hydrochloride and 2,4-dinitro-*N,N*-dimethylaniline. Attempt at dehydration of the respective quaternary salt of nicotinamide with thionyl chloride failed, too.

### Electrochemical Experiments

The electrochemical reduction of compounds *Ia-h* was carried out in three-electrode connection with mercury drop indication electrode, platinum working electrode, and saturated calomel reference electrode using the Radelkis OH 102 apparatus (Hungary). The measurements were

TABLE I  
Physico-chemical characteristics of compounds *Ia*, *Ib*, *Id*, *If*–*h*

Compound	Mol. formula (mol.mass)	Yield, % (solvent) <sup>a</sup>	M.p., °C	Calculated/Found				δ, ppm <sup>b</sup>				Note
				% C	% H	% N	% Cl	--CH <sub>2</sub> -- H-4 <sup>c</sup>	--C <sub>6</sub> H <sub>4</sub> -- H-6 <sup>c</sup>	H-5 <sup>c</sup>	H-2 <sup>c</sup>	
<i>Ia</i>	C <sub>14</sub> H <sub>13</sub> N <sub>2</sub> ClO (260.72)	67 (DMF)	171–172 dec.	64.24 64.49	5.80 5.03	9.82 10.75	13.56 13.59	5.89 s 8.95 d	7.29 q 9.23 d	8.30 t 9.48 s	<i>d</i>	
<i>Ib</i>	C <sub>14</sub> H <sub>13</sub> N <sub>2</sub> Cl (244.72)	34 (DMSO)	209 dec.	68.95 68.71	5.33 5.35	11.58 11.45	14.70 14.49	5.73 s 8.78 d	7.23 q 9.06 d	8.11 t 9.31 s	<i>e</i>	
<i>Id</i>	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> FCl (248.69)	22 (DMSO)	203–205 dec.	62.69 62.78	4.25 4.05	11.52 11.27	14.21 14.26	5.77 s 8.80 d	7.23 m 9.07 d	8.13 t 9.31 s	<i>f</i>	
<i>If</i>	C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> ClO <sub>2</sub> (288.73)	18 (DMF)	201–205 dec.	62.35 62.39	4.46 4.54	9.31 9.70	12.05 12.29	5.90 s 8.88 d	7.71 q 9.16 d	8.22 t 9.44 s	<i>g</i>	
<i>Ig</i>	C <sub>14</sub> H <sub>10</sub> N <sub>3</sub> Cl (255.71)	6 (CH <sub>3</sub> CN)	230–231 dec.	65.73 65.76	4.19 3.94	16.25 16.43	13.89 13.86	5.85 s 8.82 d	7.57 q 9.10 d	8.14 t 9.38 s		
<i>Ih</i>	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> ClO <sub>2</sub> (275.69)	3 (CH <sub>3</sub> CN)	216–217 dec.	56.44 56.64	3.96 3.66	15.15 15.24	12.63 12.86	6.00 s 9.83 d	7.86 q 9.23 d	8.30 t 9.50 s		

<sup>a</sup> The solvent in which the quaternization was carried out; <sup>b</sup> <sup>1</sup>H NMR spectra were measured in D<sub>2</sub>O with DSS as internal standard; <sup>c</sup> the protons in the pyridine nucleus; <sup>d</sup> δ = 3.81 ppm, s, OCH<sub>3</sub>; <sup>e</sup> δ = 2.18 ppm, s, CH<sub>3</sub>; <sup>f</sup> % F calculated: 7.79, found: 7.64; <sup>g</sup> δ = 7.83 ppm, s, COOCH<sub>3</sub>

carried out in a tempered polarographic vessel at 25°C under nitrogen. For the measurements in anhydrous acetonitrile, nitrogen was dried by passage through concentrated sulphuric acid and phosphorus pentoxide column. The pH measurements of the investigated solutions were carried out with a pH-Meter PAK 1 (ČSSR), using a glass electrode, after each recording of the polarographic curve. As basic electrolyte for the electrochemical measurements served the Britton-Robinson buffer (pH 1.8 to 12.0), in anhydrous acetonitrile the basic electrolyte was  $(C_2H_5)_4N^{(+)}ClO_4^{-}$ . Concentration of the depolarizers was  $1 \cdot 10^{-3}$  mol/l except for anhydrous acetonitrile: because of low solubility of compounds *Ia–h* in this solvent, saturated solutions had to be used.

The logarithmic analyses of polarographic curves were evaluated with a Hewlett-Packard 9802 table computer according to the published program<sup>16</sup>. The correlation straight lines were obtained by linear regression using a Texas Instruments computer.

## RESULTS

The polarographic reductions of compounds *Ia–h* were studied in water, 50% aqueous ethanol, and anhydrous acetonitrile. The experimental data are summarized in Table II.

*Solutions of compounds Ia–h in water:* Two waves (A and B) appear in polarograms of aqueous solutions of *Ia–g* in pH range 1–9. The A wave was characterized as an adsorption wave with half-wave potential  $-0.5$  to  $-0.6$  V (slightly shifting to negative values with increasing pH). The B wave has diffusion character. Its half-wave potential varies about  $-0.8$  V in this set of compounds, its changes with pH of solution, concentration of depolarizer, and drop period being within experimental error. Also magnitude of diffusion current remains practically unchanged within this pH range. However, shape of this wave is deformed in the region of limit diffusion current, which also makes itself felt in the logarithmic analysis of the polarographic curves (curvature). Moreover, it is obvious from slope of the straight line of the logarithmic analysis that the proper electrode process can be complicated either by a subsequent irreversible reaction or by adsorption<sup>17</sup>. The slope varies from  $1/43$  to  $1/57$   $mV^{-1}$  as compared with  $1/58$   $mV^{-1}$  for an one-electron reversible process.

Derivative *Ih* exhibits, instead of the usual adsorption pre-wave, a reduction wave of nitro group followed by B wave. However, their diffusion current ratio is 6 : 1 (suggesting thus formation of the amino derivative) instead of the expected 4 : 1 (corresponding to the usual reduction  $R-NO_2 \rightarrow R-NHOH$ )<sup>18</sup>. On ground to solutions with pH > 9.5 the polarograms are still more complicated. Besides the original waves A and B there appear two further waves C and D. The D wave with half-wave potential within the limits from  $-0.95$  to  $-1.0$  V makes, at first, a part of a double wave (together with the B wave). With time or with increasing pH of solution the height of D wave increases to the detriment of the B wave, sum of their heights being, however, almost constant.

TABLE II

Electrochemical characteristics of the B wave of reduction of compounds Ia-h in various media. Composition of the solutions measured:  $1 \cdot 10^{-3} \text{ mol l}^{-1}$  compound I or its saturated solution at 25°C (anhydrous acetonitrile), the Britton-Robinson buffer or  $0.075 \text{ mol l}^{-1}$  ( $\text{C}_2\text{H}_5\text{Li} \cdot \text{N}^+(\text{C})\text{ClO}_4^-$ ) (anhydrous acetonitrile) were used as basic electrolytes

Compound	Aqueous medium <sup>a</sup> , pH = 8.8–9.0				Water-ethanol 1 : 1, pH = 7.0–7.3				Anhydrous acetonitrile	
	$-E_{1/2}, \text{V}$	$I_d \cdot 10^6 \text{ A}$	$DT/ianF, \text{mV}^b$	$-E_{1/2}, \text{V}$	$I_d \cdot 10^6 \text{ A}$	$DT/ianF, \text{mV}^b$	$-E_{1/2}, \text{V}$	$DT/ianF, \text{mV}^b$	$-E_{1/2}, \text{V}$	$DT/ianF, \text{mV}^b$
Ia	0.818	2.47	43.3	0.798	2.11	82.7	0.801	58.9	0.801	58.9
Ib	0.811	2.52	47.9	0.791	2.08	86.0	0.795	65.2	0.795	65.2
Ic	0.822	2.62	49.4	0.775	2.14	79.0	0.824	69.5	0.824	69.5
Id	0.806	2.52	55.0	0.769	1.83	80.0	0.797	55.9	0.797	55.9
Ie <sup>c</sup>	0.815	2.12	51.2	0.781	1.69	99.9	0.771	68.1	0.771	68.1
If	0.780	2.29	54.9	0.759	1.67	85.2	0.762	55.9	0.762	55.9
Ig <sup>d</sup>	0.782	2.54	55.2	0.754	1.85	89.8	0.785	63.4	0.785	63.4
Ih <sup>e,f</sup>	0.890	0.88	—	0.825	1.74	—	0.717	36.2	0.717	36.2
							0.840	48.2	0.840	48.2

<sup>a</sup> The adsorption wave:  $E_{1/2} - 0.56$  to  $-0.59 \text{ V}$ ,  $I_d 0.11 - 0.17 \cdot 10^{-6} \text{ A}$ ; <sup>b</sup> the values calculated from logarithmic analyses of the polarographic curves; <sup>c</sup> non-readable C wave in aqueous solutions; <sup>d</sup> the C wave in aqueous solutions:  $E_{1/2} - 1.74 \text{ V}$ ,  $I_d 1.9 \cdot 10^{-6} \text{ S}$ ; <sup>e</sup> reduction of nitro group in aqueous solutions:  $E_{1/2} - 0.724 \text{ V}$ ,  $I_d 11.84 \cdot 10^{-6} \text{ A}$ ; <sup>f</sup> the polarographic maximum in aqueous solutions at  $-1.71 \text{ V}$ .

The C wave with half-wave potential ranging from  $-1.65$  to  $-1.72$  V appears on the background of separation of the basic electrolyte and is very badly readable in many cases. Value of its diffusion current varies in the investigated set of compounds, being equal to  $1/3$  (compounds *Id*, *Ie*, *If*),  $2/3$  (compounds *Ib*, *Ic*, *Ig*), and  $9/10$  (compound *Ia*) of the height of B wave measured at  $\text{pH} < 9.5$ . At  $\text{pH}$  above 11 total decomposition of the depolarizers takes place.

Nature of the depolarizers was studied by measuring UV spectra of compound *Ic* at various  $\text{pH}$  values. The original depolarizer form was found to remain unchanged up to  $\text{pH}$  9.5. In this region the UV spectra show an absorption band at 269 nm with inflexions at 264 nm and 276 nm. At  $\text{pH}$  above 9.5 new bands of low intensity appear at 309 and 356 nm. At  $\text{pH} \sim 10$  the spectra only contain two absorption bands (268 and 346 nm). At  $\text{pH}$  above 11 there appears a further inflexion at 402 nm which, however, disappears on acidification. Hence, the correlation of half-wave potentials with  $\sigma_p$  constants was carried out in the region below  $\text{pH}$  9 in which the said transformations of depolarizers do not take place (Table II).

*Solutions of compounds Ia–h in 50% aqueous ethanol:* The polarograms of the compounds *Ia–g* dissolved in 50% aqueous ethanol only exhibit the B wave in  $\text{pH}$  region from 1.0 to 8.0. Its half-wave potential is independent of  $\text{pH}$  of solution, time of drop, being only shifted to more negative potential values with increasing concentration of depolarizer (the change is 20 mV on going from  $4 \cdot 10^{-4} \text{ mol l}^{-1}$  to  $1 \cdot 10^{-3} \text{ mol l}^{-1}$  solutions). The B wave has diffusion nature. Reciprocals of slopes obtained from logarithmic analyses of the polarographic curves vary within the limits 79–100 mV which indicates an irreversible process. At  $\text{pH}$  above 8.0 the polarograms become more complicated which is analogous to the aqueous solutions. Again height of the B wave is decreased and a new D wave with half-wave potential within  $-0.95$  to  $-1.0$  V increases to the detriment of the B wave with time and increasing  $\text{pH}$ . Again sum of their heights is constant. Derivatives *Ie–g* exhibit the C wave or maximum at potentials  $-1.65$  to  $-1.78$  V, its height being smaller or approaching to the magnitude of B wave. In contrast to aqueous solutions, in ethanolic media there further appears an E wave at the potentials  $-1.2$  to  $-1.3$  V, its height being increased with time, too. On going to solutions with  $\text{pH}$  above 10.5 there takes place complete decomposition of the depolarizers, and the polarographic record becomes less clear.

Reduction of compound *Ih* proceeds in two waves. The B wave is of similar nature to that of the other derivatives. Besides, the polarograms contain a reduction wave of nitro group whose half-wave potential is shifted to more negative potentials with increasing  $\text{pH}$  ( $\Delta E_{1/2}/\text{pH} = 55 \text{ mV}$ ). Ratio of diffusion currents of this wave and the B wave is 4 : 1, which indicates reduction of nitro group of the respective hydroxylamino derivative (see ref.<sup>18</sup>).

Compounds *Ia–h* are only stable in acid and neutral solutions, *i.e.* upto  $\text{pH}$  8.0,

when UV spectrum of, *e.g.*, compound *Ic* exhibits two overlapping bands at 264 and 268 nm and an inflexion at 274 nm. pH Increase to 9.5 changes the spectrum: there appear absorptions at 239, 245, 309, and 352 nm. The said change at this pH value are reversible except for the last absorption band of low intensity which, in addition thereto, is shifted to higher wavelengths (371 nm). Analogous changes can be found above pH 9.5, they are, however, irreversible with increasing pH. Strongly alkaline solutions (pH  $\sim$  12) have characteristic absorptions at 266 and 347 nm and an inflexion at 410 nm. The said pH changes of compound *Ic* in aqueous ethanolic solutions are represented in Fig. 1.

*Solutions of compounds Ia–h in anhydrous acetonitrile:* Polarograms of compounds *Ia–g* in anhydrous acetonitrile medium only exhibit the B wave of diffusion nature which follows from dependence of the diffusion current on the reservoir height. Reciprocals of slopes of straight lines of logarithmic analyses of the polarographic curves vary within the limits 56–69 mV, which indicates an one-electron reversible process. Reduction of the nitro derivative is somewhat more complicated. Four waves can be seen in the polarogram at  $-0.71$ ,  $-0.84$ ,  $-1.19$ , and  $-1.41$  V, ratio of their heights being 1.0 : 1.2 : 3.0 : 2.2. Way of the reduction of nitro derivative is explained in Discussion.

## DISCUSSION

It can be seen from the given results of study of aqueous solutions of compounds *Ia–g* that their behaviour is analogous to that reported<sup>2,3</sup> for 1-methyl-3-cyanopyridinium iodide, for B and C waves corresponding to A and B waves of ref.<sup>3</sup>, respectively. In addition thereto, the pre-wave A is observed as an adsorption wave, which is probably connected with higher adsorptivity of 1-benzyl cations at the surface

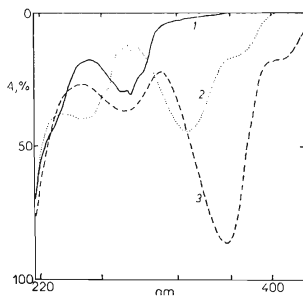
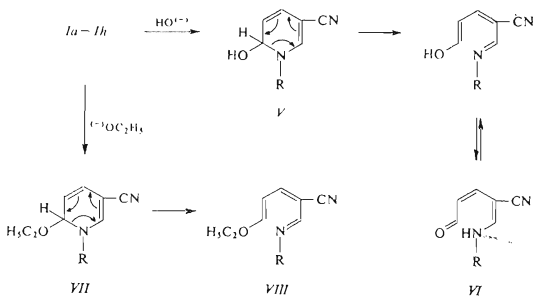


FIG. 1  
UV Spectra of compound *Ic* measured at various pH values (1–13) in 50% aqueous ethanol: 1 pH below 8; 2 pH 9.5; 3 pH 12.2

of dropping mercury electrode in accordance with occurrence of analogous waves in polarography<sup>1</sup> of 1-benzyl-3-carbamoylpyridinium salts. However, different behaviour of the depolarizers *Ia-h* from that of the above-mentioned ones consists in general shift of the half-wave potentials to positive values by about 108–221 mV and in the fact that the polarographic behaviour can be easily interpreted up to pH about 9 where the *B* wave can be assigned unambiguously to formation of radicals *II* ( $R = p\text{-XC}_6\text{H}_4\text{CH}_2$ ), and the other wave *C* can be assigned to reduction down to the stage of dihydropyridine *III* or *IV* ( $R = p\text{-XC}_6\text{H}_4\text{CH}_2$ ). Above pH 9.5 the present nucleophiles add to the ions *Ia-g* (because of the increased electron affinity of pyridine nucleus due to the effect of 3-cyano group), which results in formation of further waves (*D* and *E*) corresponding to the chemical artifacts. Scheme 1 gives a probable explanation of these processes based on kinetic



SCHEME 1 ( $R = p\text{-X-C}_6\text{H}_4\text{-CH}_2$ )

changes observed in UV spectra of *Ia-h* salts solutions and illustrated in Fig. 1 for *Ic* depolarizer. Consequently, the primary attack by  $\text{OH}^-$  and  $\text{C}_2\text{H}_5\text{O}^-$  ions in aqueous and aqueous-ethanolic media, respectively, leads to the polarographically inactive dihydropyridines *V* and *VII* which can be assigned to the absorption maxima at 310 and 340 nm in the UV spectra. Their electrocyclic transformation (see analogous cases<sup>19</sup>) leads to the polarographically active valence isomers *VI* and *VIII* which are obviously connected with the little intensive long-wave absorption maxima at 370 to 420 nm and with the *D* and *E* waves in the polarographic curves. It cannot be excluded that some further artifacts (similar to the products isolated<sup>19</sup> after alkaline decomposition of 1-methyl-3-cyanopyridinium iodide) participate in this complex polarographic behaviour observed at higher pH values.

In accordance with the above-given interpretation, the electroreduction of compounds *Ia-g* in anhydrous acetonitrile proceeds in a single wave *B*, because the



adsorption connected with the *A* wave is obviously suppressed, and the *C* wave corresponds to a process necessitating the proton which is not present in the aprotic medium.

Partly different behaviour is encountered with the *p*-nitro derivative *Ih* in all the studied solutions, the above-mentioned waves being accompanied by further waves of independent reduction of the *X* substituent. From this point of view the least clear situation is that in anhydrous acetonitrile, so the polarographic behaviour of compound *Ih* in this solvent was confronted with reduction of the corresponding 3-carbamoylpyridinium salt<sup>1</sup> and *p*-nitrotoluene. Table III shows that these three compounds undergo reduction of nitro group in two waves in the potential range  $-1.1$  to  $-1.8$  V, hence the remaining waves at more positive potentials can be assigned *per analogiam* to reduction of heterocyclic section of the depolarizers, *i.e.* to the wave of *B* type.

Effects of the *X* substituents on half-wave potentials of the *B* waves of the compound series *Ia-h* are less distinct and not so easily interpreted as compared with the earlier findings<sup>1</sup> concerning the 3-amidic series. In aqueous and aqueous-ethanolic media no reproducible quantitative parallel could be found between the two series. Only the solutions in anhydrous acetonitrile show a more distinct correlation trend, however, with some exceptions (Fig. 2). Above all striking is the deviation for the substituents *X* = CH<sub>3</sub> and CN. The groups CONH<sub>2</sub> and CN at 3 position seem to cause different orientation of the depolarizer cations at the surface of mercury electrode, which could be manifested most distinctly just in the effect of the van der Waals interactions with such *X* substituents which most resemble the solvent molecules, *i.e.* CH<sub>3</sub>CN. Another ambiguity consists in the fact that reduction of heterocyclic section of ion *Ih* proceeds distinctly in two waves *B*<sub>1</sub> and *B*<sub>2</sub> with the half-wave

TABLE III

Comparison of half-wave potentials of depolarizers of general formula  $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{X}$  measured<sup>a</sup> in anhydrous acetonitrile

Molecular fragment <i>X</i>	<i>B</i> wave $-E_{1/2}$ , V	NO <sub>2</sub> wave $-E_{1/2}$ , V	Rel. height <sup>b</sup> B/NO <sub>2</sub>
H	—	1.305 1.745	—
3-Cyano-1-pyridinium chloride	0.708 0.836	1.192 1.412	0.417
3-Carbamoyl-1-pyridinium chloride	0.878 —	1.155 1.385	0.407

<sup>a</sup> See Experimental; <sup>b</sup> ratio of the height sums of the two types of waves.

potential values  $-0.708$  and  $-0.846$  V (Table III). The half-wave potential value of the  $B_1$  wave correlates well with analogous data for the  $B$  wave of the other members of the series  $Ia-g$ , but the half-wave potential value of the  $B_2$  wave deviates considerably. It is presumed that the occurrence of the two waves  $B_1$  and  $B_2$  is again connected with the orientation effects of the depolarizer  $Ih$  rather than with a change in the reduction mechanism. This presumption is supported by the fact that detailed

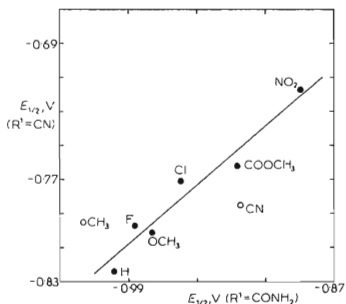


FIG. 2

Relation of  $E_{1/2}$  of the reduction wave  $B$  of 1-( $p$ -substituted benzyl)-3- $R^1$ -pyridinium chlorides in anhydrous acetonitrile

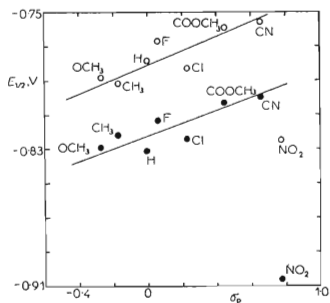


FIG. 3

Correlation of  $E_{1/2}$  of the reduction  $B$  wave of compounds  $I$  with  $\sigma_p$  constants<sup>21</sup>. Aqueous solutions, pH 8.8–9.0,  $\circ$   $H_2O$ - $EtOH$  (1 : 1), pH 7.0–7.3

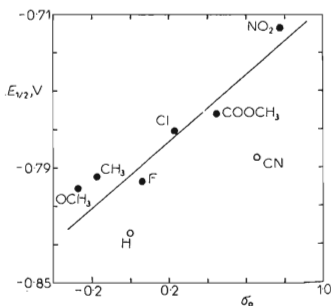


FIG. 4

Correlation of  $E_{1/2}$  of the reduction  $B$  wave of compound  $I$  in anhydrous acetonitrile with  $\sigma_p$  constants<sup>21</sup>. The meaning of the points see Fig. 3

analysis of the shape of the *B* wave with the half-wave potential  $-0.878$  V for 1-(*p*-nitrobenzyl)-3-carbamoylpyridinium chloride (Table III) shows a most likely superposition of two waves (analogous to the  $B_1$  and  $B_2$  types) having, however, very close half-wave potentials.

Correlation of the half-wave potential values of the *B* wave with the Hammett  $\sigma_p$  constants in the series *Ia-h* shows qualitative similarity to that of the 3-amidic analogues<sup>1</sup>. The  $\varrho_{\pi,R}$  values found for aqueous and aqueous-ethanolic media are 0.031 ( $r = 0.838$ ) and 0.037 ( $r = 0.864$ ), respectively, *i.e.* they are lower, and, besides, the half-wave potential of compound *Ih* ( $X = \text{NO}_2$ ) strongly deviates due to pre-C-deprotonation<sup>1,20</sup> (Fig. 3). On the contrary, the value  $\varrho_{\pi,R} = 0.077$  ( $r = 0.952$ ) was found for the solutions in anhydrous acetonitrile, distinct deviations being observed for the substituent  $X = \text{CN}$  and for the non-substituted member *Ic* of the series (Fig. 4).

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Translated by J. Panchartek.