

**POLAROGRAPHIC REDUCTION OF *p*-SUBSTITUTED 1-PHENYL-3-AMINOCARBONYLPYRIDINIUM SALTS**Jiří KRECHL<sup>a</sup>, Daniela MIŽANINOVÁ<sup>a</sup>, Jiří VOLKE<sup>b</sup> and Josef KUTHAN<sup>a</sup><sup>a</sup> Department of Organic Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6,<sup>b</sup> The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 118 40 Prague 1

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The substitution effect of different groups (H, NO<sub>2</sub>, COOH, Br, Cl, NHCOCH<sub>3</sub>, CH<sub>3</sub>, OCH<sub>3</sub>, OH, and N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>) on the polarographic behaviour of *p*-substituted 1-phenyl-3-aminocarbonylpyridinium cations has been investigated, in particular on their half-wave potentials in aqueous phosphate buffers pH 6.65 (10% DMF) and in anhydrous solutions of dimethylformamide with 0.05 mol l<sup>-1</sup> (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> as supporting electrolyte. The half-wave potentials of the reduction wave which corresponds to the uptake of a single electron (wave B) and to the formation of the primary radical, obey a Hammett correlation in a similar way as it is in the case of 1-benzyl-3-aminocarbonylpyridinium cations. The slope  $\rho_{\pi,R}$  in the Hammett plot equals 0.093 V for 10% DMF and 0.179 V for anhydrous DMF and compares thus with this slope obtained with the 1-benzyl derivatives where 0.095 V was found for water and 0.127 V for anhydrous acetonitrile. The transfer of the substitution effect from the substituent in the *para* position on the benzene nucleus to the heterocyclic ring is thus equally active in both substances and depends more strongly on the solvent than on the structure of cations of both types. The low sensitivity in both series towards a change in the substituent is explained by the fact that during the uptake of the electron the benzene and the pyridine nucleus are not even approximately coplanar. This is why the  $\pi$ -overlap between the two nuclei is considerably restricted. The analysis of sampled dc-polarographic waves has confirmed that the one-electron uptake is followed by a chemical reaction, most probably a dimer formation or a reaction of the primary product with the starting substance.

1,3-Disubstituted quaternary pyridinium salts are interesting as simple bioorganic models of NAD(P) coenzymes. The electrochemical reduction of the corresponding cations can inform us about the ability of these models to accept electrons from the immobilized substrate which in the first approximation can be represented by a dropping mercury electrode. A useful approach to the investigation of such an electron transfer mechanism proved to be a quantitative research of the substitution effect<sup>1-3</sup>. An application of the Hammett correlation<sup>4</sup> (*A*) to the half-wave potentials in case of *p*-substituted 1-benzyl-3-aminocarbonylpyridinium chlorides *Ia,c,d,f,g,i-1* pointed<sup>2</sup> to the relatively low sensitivity of the followed potentials toward a change in the substituent X ( $\rho_{\pi,R} = 0.061$  to 0.127 V) and to a strongly different behaviour of



in 40 ml methanol and the resulting mixture was heated at a temperature corresponding to the boiling point. Then the solvent was removed *in vacuo*, the residue stirred with 40 ml of water and the insoluble part filtered off. The filtrate was repeatedly extracted with chloroform and the aqueous phase evaporated to dryness *in vacuo*. The residue was recrystallized from a minimum quantity of methanol, the obtained crystals of the product were washed with ether and repeatedly recrystallized from methanol. The yields of salts *IIa–j* obtained in this way and their melting points are given in Table I.

#### 4'-X-Phenyl-3-aminocarbonylpyridinium Perchlorates (*IIIa–j*)

6 mmol of the corresponding chloride *II* were dissolved in a minimum volume of warm water and to the solution thus formed an excess of diluted perchloric acid was added. If colourless crystals were precipitated they were redissolved by repeatedly heating the solution. After cooling down the solution the crystals of the corresponding perchlorate *III* were sucked off and recrystallized from water. Because of difficulties connected with refining it was impossible to obtain the derivatives *IIIe,i* in pure state. The yields and physical constants of salts *IIIa–d, f–h,j* obtained in this way are summarized in Table II.

#### Electrochemical Experiments

Polarographic measurements were effectuated with a three-electrode circuit. A dropping mercury electrode with an outflow velocity equal to  $2.62 \text{ mg s}^{-1}$  was applied as a working electrode, a platinum foil served as a counter-electrode and an Ag/AgCl electrode was the reference electrode. These electrodes jointly with the polarographic cell were components of the electrode stand of the static electrode SMDE 1 but the working electrode was adapted for a free mercury outflow from the capillary at a controlled drop-time.

The measurements were carried out on the polarographic analyzer PA 4 with the XY recorder 4105 in the sampled polarography mode (*i.e.* fast polarography), the scan rate being  $2 \text{ mV s}^{-1}$  in the direction from 0.0 V to more negative potentials and the sensitivity 250 nA/cm for aqueous media and 500 nA/cm for measurements in non-aqueous media. The drop-times (2 s aqueous and 1 s in non-aqueous media) were controlled by a time-beater in the stand of the static electrode SMDE 1.

Polarographic data were measured with solutions of the studied salts *II* and *III* in 10% aqueous and in non-aqueous dimethylformamide. The supporting electrolyte in the aqueous solvent was a  $0.07 \text{ mol l}^{-1}$  phosphate buffer according to Michaelis (pH = 6.65) and for measurements in the non-aqueous media the quarternary salt  $0.05 \text{ mol l}^{-1} (\text{n-C}_4\text{H}_9)_4^+\text{BF}_4^-$  was made use of. The concentrations of the depolarizer in aqueous DMF were from  $2 \cdot 10^{-4}$  to  $1 \cdot 10^{-3} \text{ mol l}^{-1}$ , in anhydrous DMF then  $5 \cdot 10^{-4}$  to  $1.5 \cdot 10^{-3} \text{ mol l}^{-1}$ . Before recording the *i–E* curve the investigated solutions were first deaerated by a stream of nitrogen or, more often, of argon; during recording the curve the inert gas was led above the solution.

The half-wave potentials  $E_{1/2}$  were obtained either by directly evaluating the *i–E* curves and, for substances *IIIa–d, f–h* (anhydrous dimethylformamide) also from the logarithmic plots ( $\log i/(i_d - i)$  vs *E*) of these curves. The comparison of values of  $E_{1/2}$  obtained by this procedure is visible for substances *IIIa–d, f–h, IIe,i* in Table III. The same table also includes the values of the slopes  $RT/anF$  bearing relation to the reversibility of the electrode processes followed in this paper. The correlations (*A*) making use of the substitution constants<sup>6</sup> of substituents X were evaluated by regression analysis with the help of a program built-in in the pocket calculator Sharp E 512, *cf.* Figs 1 and 2.

TABLE I  
Physical characteristics of 4'-X-phenyl-3-aminocarbonylpyridinium chlorides *Ila-j*

Substance	Substituent	Summary formula M g mol <sup>-1</sup>	Melting point °C	Yield %	Elemental analysis calculated/found			
					% C	% H	% N	% Cl
<i>Ila</i>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	C <sub>16</sub> H <sub>20</sub> N <sub>3</sub> OCl 305.8	143—146	12	62.84 62.72	6.60 6.81	13.74 13.79	11.59 11.30
<i>Ilb</i>	OH	C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> Cl 250.7	237—239	35	57.50 57.47	4.42 4.41	11.18 11.26	14.14 14.20
<i>Ilc</i>	OCH <sub>3</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> Cl 264.7	235—237	40	58.99 58.85	4.95 4.98	10.58 10.75	13.39 13.42
<i>Ild</i>	CH <sub>3</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> OCl 248.7	209—212	39	62.78 62.46	5.27 5.48	11.26 11.52	14.26 14.58
<i>Ile</i>	NHCOCH <sub>3</sub>	C <sub>14</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> Cl 291.7	abowe 350	42	57.64 57.56	4.84 5.01	14.40 14.13	12.15 12.00
<i>IIf</i>	H	C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> OCl 234.7	242—243	43	61.42 61.13	4.72 4.83	11.94 11.62	15.10 15.35
<i>Ilg</i>	Cl	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> OCl <sub>2</sub> 269.1	287—289	43	53.55 53.92	3.75 3.96	10.41 10.67	26.35 26.13
<i>Ilh<sup>a</sup></i>	Br	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> OBrCl 313.6	abowe 350	9	45.96 45.81	3.22 3.48	8.93 9.16	11.31 11.77
<i>Ili</i>	COOH	C <sub>13</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> Cl 278.7	abowe 300	24	56.03 56.02	3.98 4.01	10.05 10.03	12.72 12.80
<i>Ilij</i>	NO <sub>2</sub>	C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> Cl 279.7	162—164	10	51.53 51.18	3.60 3.71	15.03 15.51	12.68 12.47

<sup>a</sup> % Br: calculated 25.48, found 25.14.

TABLE II  
Physical characteristics of 4'-X-phenyl-3-aminocarbonylpyridinium perchlorates IIIa-d, f-h, j

Substance	Substituent	Summary formula M g mol <sup>-1</sup>	Melting point, °C		Yield %	Elemental analysis calculated/found			
			found	literature <sup>b</sup>		% C	% H	% N	% Cl
IIIa <sup>a</sup>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	C <sub>16</sub> H <sub>21</sub> N <sub>3</sub> O <sub>9</sub> Cl <sub>2</sub> 470.3	227-229	—	43	40.87	4.50	8.94	15.08
IIIb <sup>b</sup>	OH	C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> O <sub>6</sub> Cl 314.7	203-204	—	64	45.80	3.52	8.90	11.27
IIIc	OCH <sub>3</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> O <sub>6</sub> Cl 328.7	231-232	232-233	77	47.50	3.99	8.52	10.79
III d	CH <sub>3</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> O <sub>5</sub> Cl 312.7	228-230	232-233	77	49.93	4.19	8.97	11.34
III f	H	C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> O <sub>5</sub> Cl 298.7	190-193	190-192	79	48.26	3.71	9.38	11.87
III g	Cl	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub> Cl <sub>2</sub> 333.1	259-261	—	81	43.27	3.03	8.41	21.28
III h	Br	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub> ClBr 377.6	265-267	263-265	58	43.53	3.23	8.53	21.04
III j	NO <sub>2</sub>	C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> O <sub>7</sub> Cl 343.7	144-146	—	38	41.94	2.93	12.23	32.29
						41.89	2.91	12.62	32.04

<sup>a</sup> 1-(4'-Diethylammoniumphenyl)-3-carbamoylpyridinium diperchlorate; <sup>b</sup> % Br: calculated 21.16, found 20.85%.

TABLE III

Half-wave potentials and slopes of polarographic waves (from the log plot) of *IIIa-d, f-h, IIe, i* in anhydrous DMF for  $1.5 \cdot 10^{-3} \text{ mol l}^{-1}$  depolarizer,  $0.025\text{M}-(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{BF}_4^-$

Substance	Substituent	$-E_{1/2}^a, \text{V}$	$-E_{1/2}^b, \text{V}$	$RT/anF^c$ mV
<i>IIIa</i> <sup>d</sup>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	0.965	0.955	110
<i>IIIb</i>	OH	0.910	0.908	38
<i>IIIc</i>	OCH <sub>3</sub>	0.905	0.902	42
<i>IIId</i>	CH <sub>3</sub>	0.890	0.887	44
<i>IIe</i>	NHCOCH <sub>3</sub>	0.890	0.890	45
<i>IIIf</i>	H	0.865	0.868	42
<i>IIIg</i>	Cl	0.820	0.816	53
<i>IIIh</i>	Br	0.805	0.808	52
<i>IIIi</i>	COOH	0.760	0.756	46

<sup>a</sup>  $E_{1/2}$  read from the dc-polarographic curve; <sup>b</sup>  $E_{1/2}$  calculated from the log plot; <sup>c</sup> the values of slopes calculated from the log plot; <sup>d</sup> 1-(4'-diethylammoniumphenyl)-3-carbamoylpyridinium diperchlorate.

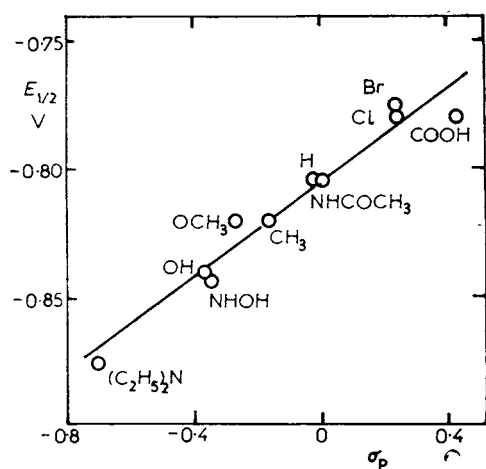


FIG. 1

Correlation of  $E_{1/2}$  for the reduction of *IIa-j* in 10% DMF with  $\sigma_p$  substituent constants of X

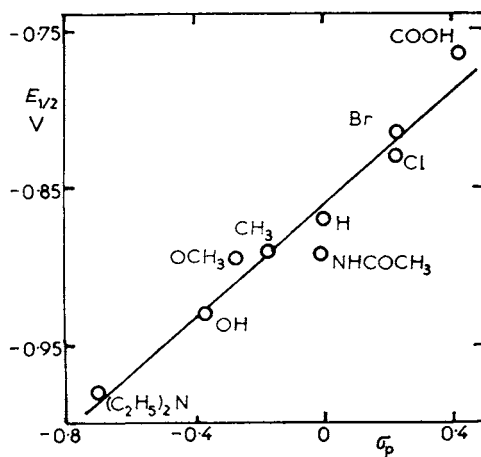
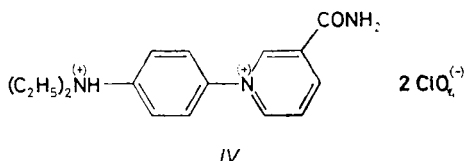


FIG. 2

Correlation of  $E_{1/2}$  for the reduction of *IIIa-d, f-h, IIe, i* in anhydrous DMF with  $\sigma_p$  substituent constants of X

## RESULTS

Polarographic measurements were performed with solutions of chlorides *Ila–j* in aqueous 10% DMF and with perchlorates *IIla–d, f–h, j* in anhydrous DMF. Since the attempts to prepare the pure perchlorate *IIla* only led to the corresponding bis-perchlorate *IV*



the measurements in DMF were made with this sample. Fortunately, it was found that in this case the basicity of the solvent enables the following deprotonation:



consequently – owing to a large excess of DMF – the actually at the electrode reacting particle was prevalently a monocation of the perchlorate *IIla*.

For comparison the polarographic properties of the formerly investigated<sup>2</sup> 4'-benzyl derivatives *Ic, d, f, g* were also measured (*cf.* Table IV).

All depolarizers described in this paper exhibit an analogous polarographic behaviour: adsorption prewaves A in the more positive region and diffusion-controlled one-electron waves B over the more negative potential region. A further, still more negative wave C which had been in some cases<sup>2</sup> observed with aqueous and water–ethanolic solutions of chlorides *I*, could not be interpreted because of interference caused by reduction of the components of the base solution.

*Solutions of Ila–j Salts in Aqueous Dimethylformamide (cf. Table IV)*

It was found that for aqueous solutions the  $E_{1/2}$  values are virtually pH-independent within the pH region from 4.6 to 9.2. By adding DMF to the solutions of *IIa–j* in buffers pH 6.65 the  $E_{1/2}$ -values are shifted to somewhat more positive values. The height and the position of the more positive wave A did not vary with increasing the depolarizer concentration. On the other hand, the main one-electron waves B are unambiguously diffusion-controlled, their height increases as a liner function with the concentration of the compound to be investigated and is a linear function of the square root of the height of the mercury head. With increasing concentration, both waves, A and B, are slightly shifted to more negative potentials. In case of the 4'-diethylamino derivative *IIa* one may observe in addition to A and B a further low

diffusion-controlled wave A' of unknown origin; its  $E_{1/2}$  is  $-0.405$  V. The 4'-nitro derivative *IIj* exhibits further two waves of fourfold height besides A and B, due to the electrochemical reduction<sup>7</sup> of the substituent X.

*Solutions of salts IIIa–d, f–h, j, IIe, i in anhydrous DMF*

Because of their poor solubility and difficulties connected with their refining the polarographic curves of perchlorates *IIIe, i* could not be recorded and this is why they are replaced in the studied series by the corresponding chlorides *IIe, i*. The sampled dc-polarograms of all studied depolarizers exhibited exclusively a one-electron diffusion-controlled wave B except for *IIe, i* in which, starting from  $+0.4$  V anodic waves of chlorides can be observed. In case of the 4'-nitroderivative *IIIj* wave B coincides with the waves corresponding to the reduction of the substituent X( $\text{NO}_2$ ) so that the dc-polarographic characteristics could be only estimated and are therefore not included in Table V.

TABLE IV

Polarographic reduction of *IIa–j* and *Ic, d, f, g* in 10% aqueous DMF. Depolarizer concentration  $5 \cdot 10^{-4}$  mol l<sup>-1</sup> in 0.07M-phosphate buffer according to Michaelis (pH = 6.65)

Substance	Substituent	$i_1 \cdot 10^6, \text{A}$		$-E_{1/2}, \text{V}$	
		A	A + B	A	A + B
<i>IIa</i>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	—	0.625 <sup>a</sup>	—	0.875
<i>IIb</i>	OH	0.163	1.650	0.690	0.840
<i>IIc</i>	OCH <sub>3</sub>	0.175	1.694	0.648	0.820
<i>Ic</i>		0.188	1.513	0.768	0.917
<i>IIId</i>	CH <sub>3</sub>	0.163	1.475	0.635	0.820
<i>Id</i>		0.150	1.413	0.765	0.935
<i>IIe</i>	NHCOCH <sub>3</sub>	0.100	1.400	0.595	0.805
<i>IIf</i>	H	0.175	1.063	0.650	0.805
<i>If</i>		0.200	1.513	0.790	0.930
<i>IIg</i>	Cl	0.163	1.375	0.550	0.780
<i>Ig</i>		0.213	1.738	0.720	0.900
<i>IIh</i>	Br	0.150	0.910	0.535	0.775
<i>IIIi</i>	COOH	0.150	1.375	0.673	0.780
<i>IIj</i>	NO <sub>2</sub>	0.350	5.000 <sup>b</sup>	0.350	0.845

<sup>a</sup> Two small prewaves appear on the polarograms. <sup>b</sup> The value of the diffusion current of an independent wave which is preceded by one more wave of approximately equal height at  $E_{1/2} = -0.500$  V and with  $i_1 = 4.6 \cdot 10^{-6}$  A.



Solutions of Salts *Ic, d, f, g* in Anhydrous DMF

The experimental polarographic data are compared in Table VI. It is obvious that these compounds behave in an analogous manner as the corresponding phenyl derivatives *III*.

TABLE V

Polarographic reduction of *IIIa-d, f-h, IIe,i* in anhydrous DMF. Depolarizer concentration  $10^{-3} \text{ mol l}^{-1}$ , supporting electrolyte  $0.025\text{M}-(\text{C}_4\text{H}_9)_4\text{N}^+\text{BF}_4^-$

Substance	Substituent	Wave B $i_1 \cdot 10^6, \text{ A}$	$-E_{1/2}, \text{ V}$	$RT/anF^a$ mV
<i>IIIa</i> <sup>b</sup>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	6.100	0.980	110
<i>IIIb</i>	OH	2.700	0.930	38
<i>IIIc</i>	OCH <sub>3</sub>	3.950	0.895	42
<i>III d</i>	CH <sub>3</sub>	2.675	0.890	44
<i>IIe</i>	NHCOOCH <sub>3</sub>	2.150	0.895	45
<i>III f</i>	H	3.450	0.870	42
<i>III g</i>	Cl	3.300	0.830	53
<i>III h</i>	Br	3.500	0.815	52
<i>III i</i>	COOH	2.900	0.765	46

<sup>a</sup> Slopes calculated from logarithmic plots; <sup>b</sup> 1-(4'-diethylammoniumphenyl)-3-carbamoyl diperchlorate.

TABLE VI

Comparison of polarographic characteristics of *IIIc,d,f,g* and *Ic,d,f,g* for the reduction in anhydrous DMF at  $10^{-3} \text{ mol l}^{-1}$  depolarizer concentration; supporting electrolyte  $0.025\text{M}-(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{BF}_4^-$

Substance	Substituent	$i_1 \cdot 10^6, \text{ A}$	$-E_{1/2}, \text{ V}$
<i>IIc</i>	OCH <sub>3</sub>	3.950	0.895
<i>Ic</i>		3.075	1.055
<i>II d</i>	CH <sub>3</sub>	2.675	0.890
<i>Id</i>		0.925 <sup>a</sup>	1.070
<i>II f</i>	H	3.450	0.870
<i>If</i>		3.350	1.030
<i>II g</i>	Cl	3.300	0.830
<i>Ig</i>		3.610	1.015

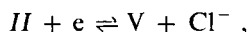
<sup>a</sup> Considerably decreased solubility of depolarizer in DMF.

*Cyclic Voltammetry of Compounds IIIa–d, f–h, j*

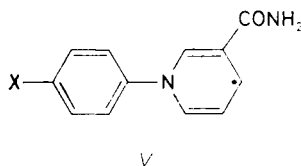
The measurements were carried out with a hanging mercury electrode at a scan rate  $\leq 50 \text{ V s}^{-1}$ . Under these conditions, we did not succeed in detecting an anodic peak corresponding to the oxidation of the primary product which resulted in the reduction of the compound in wave B.

## DISCUSSION

It follows from the above findings that under given conditions the quarternary cations of salts *II* and *III* undergo the following one-electron reductions at a dropping mercury electrode:



this occurs at the potential of wave B and the polarographic data do not yield direct information about the fate of the primarily formed radicals *I*, since because of the solubility of the studied compounds and because of the technical properties of the modified static mercury drop electrode it was not possible to investigate the dependence of the polarographic one-electron waves on the concentration of the studied compound *c* and on the drop-time  $t_1$ . The one-electron character of the process follows unambiguously from a comparison of the wave-heights B in the phenyl derivative *II* and *III* with those of the corresponding benzyl derivatives *I* for which the one-electron reduction has been earlier confirmed<sup>2</sup>. The fact that cyclic voltammetry has not given any information about the oxidation of the particles *V* can be explained by their very fast follow-up reaction, most probably leading to the electrochemically inactive dimers<sup>8–12</sup>. This also strongly disturbs the reversibility in the formation of the



particles *V* in agreement with the results of log plots of dc-polarographic curves in  $\log i/(i_1 - i) - E$  coordinates. As follows from Table III their slope  $RT/\alpha nF$  is as a rule somewhat lower than would correspond to the assumed value 59 mV for a single-electron process (with the exception of the 4'-diethylamino derivative *IIIa*).

It follows from Figs 1 and 2 that the half-wave potentials  $E_{1/2}$  for wave B in compounds *IIa–i* and *IIIa–d, f, h* exhibit a rather good Hammett correlation (*A*) with

substitution parameters<sup>6</sup>  $\sigma_p$  ( $r = 0.974$  or  $0.975$  for 10 or 9 values, respectively). The values of  $\rho_{\pi,R}$   $0.093$  V (with 10% DMF) or  $0.179$  V (with anhydrous DMF) are rather low, however, and comparable with the analogous slopes<sup>2</sup> obtained with the benzyl derivatives *I*,  $0.095$  V (water) and  $0.127$  V (anhydrous acetonitrile). This points to the fact that the transfer of the substitution effect from the group X to the heterocyclic nucleus is approximately equally efficient in the series of salts *I–III* and its magnitude depends more on the solvent than on the difference in the structure of the cations in the salts *II*, *III*, and *I*. The relatively low sensitivity in the series *II* and *III* toward a variation in the substituent X can be explained by the situation that during the measurement the pyridine and benzene rings in the double layer are not even approximately coplanar and the  $\pi$ -overlap between the two cyclic systems is to a considerable degree eliminated.

An uncertainty in the correlations represented in Figs 1 and 2 is evoked by inserting the points for 4'-nitroderivatives *IIj* and *IIIj*, where in the polarographic measurements a reduction of the nitro group<sup>7</sup> occurs according to the equation  $\text{Ar}-\text{NO}_2 + 4e + 4\text{H}^+ \rightarrow \text{Ar}-\text{NHOH} + \text{H}_2\text{O}$ . When using the value  $\sigma_p + 0.81$  for the nitro group, this point is located outside the correlation straight lines in the direction toward the negative values of  $E_{1/2}$ . This behaviour, however, is not unusual.

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