POLAROGRAPHIC REDUCTION OF p-SUBSTITUTED 1-BENZYL-3-CARBAMOYLPYRIDINIUM CHLORIDES

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Substituent effects (H, NO$_2$, CN, COOCH$_3$, CH$_3$, CH$_3$O, (CH$_3$)$_2$N, Cl, F) on polarographic characteristics of the title quaternary salts have been studied in water, anhydrous acetonitrile, and aqueous ethanol. In the last solvent a gradual disappearance of one of the polarographic waves takes place. Probable course of the investigated electrode processes and accompanying chemical transformations is discussed.

Quaternary salts of nicotinamide (*II*) are interesting as bioorganic models of NAD coenzyme. Within studies of reactivity and mechanism of chemical transformations of these compounds their polarographic reduction was also investigated[1-3]: they give two one-electron waves whose formation was convincingly explained recently[4-6]. In the said type of compounds substituent effects on polarographic characteristics were investigated with the compounds carrying various substituents at 1 and 3 positions of the pyridine nucleus[7]. Furthermore, we have only found in literature limited information on slight effects of various alkyl substituents at the heterocyclic nitrogen atom[8] and effects of length of their carbon chain on half-wave potentials of the both waves[9].

The aim of the present communication is study of behaviour of the quaternary salts *Ia*−*i* during polarographic reduction of their solutions at the mercury dropping electrode and detailed investigation of influence of substituents X on the processes studied.

When preparing the studied salts *Ia*−*i* by means of quaternization[10] of amide *II* with the corresponding benzyl chlorides we failed to obtain compound *Ii* due to extreme lability[11] of p-dimethylaminobenzyl halogenides. Therefore, we tried to synthetize the salt *Ii* by two different alternative ways. One of them made use of the so called "Zincke salt" of nicotinamide *III* which gave − as in some analogous cases[12] − the required product *Ii* in good yield by the reaction *III* + *IV* → *Ii* + 2,4-(NO$_2$)$_2$.C$_6$H$_3$NH$_2$. The other way was based on the known[11] transamination of p-dimethylaminobenzyldimethylamines by other tertiary amines on action of benzoyl chloride, *i.e.* in our case on the reaction *II* + *V* + C$_6$H$_5$COCl → *Ii* + C$_6$H$_5$CON(CH$_3$)$_2$ which, however, gave the product *Ii* in a mixture with another not easily separable substance and thus proved to be less suitable for preparative purposes.

EXPERIMENTAL

The temperature data are not corrected. The spectral characteristics were measured with a Perkin Elmer 325 and a Varian XL 100 apparatus. The spectral and elemental analyses were carried out in Central laboratory of our Institute.

Syntheses of the Used Substances

The known 1-benzyl-3-carbamoylpyridinium chlorides *Ia, Ib, Ie, If* and *Ih* were prepared by quaternization[13] of nicotinamide (*II*) with the corresponding benzyl chlorides. All the products gave satisfactory results of elemental analyses and showed the following melting points (°C): *Ia* 244 (ref.[14]: 238); *Ib* 212 (213—214)[13]; *Ie* 275 (266—268)[13]; *If* 258—260 (260—262)[13]; *Ih* 236—237 (229—231)[13]. The yet non-described quaternary salts *Ic, Id* and *Ig* were prepared analogously by heating the starting reaction components in the respective solvent for 2—3 h; the raw products were crystallized from 50% aqueous ethanol. The quaternization in methanol gave 27% 1-(4-cyanobenzyl)-3-carbamoylpyridinium chloride (*Ic*), m.p. 286—288°C. For $C_{14}H_{12}N_3OCl$ (273·7) calculated: 61·43% C, 4·42% H, 12·93% Cl, 15·35% N; found: 61·10% C, 4·69% H, 12·67% Cl, 15·70% N. The quaternization in methanol gave 20% 1-(4-methoxycarbonylbenzyl)-3-carbamoylpyridinium chloride (*Id*), m.p. 272°C. For $C_{15}H_{15}N_2O_3Cl$ (306·7) calculated: 58·73% C, 4·93% H, 11·56% Cl, 9·13% N; found: 58·98% C, 5·13% H, 11·95% Cl, 8·92% N. The quaternization in ethanol gave 83% 1-(4-methylbenzyl)-3-carbamoylpyridinium chloride (*Ig*), m.p. 256—257°C. For $C_{14}H_{15}N_2OCl$ (262·7) calculated: 64·00% C, 5·76% H, 13·49% Cl, 10·66% N; found: 64·02% C, 5·76% H, 13·50% Cl, 10·64% N.

1-(4-Dimethylaminobenzyl)-3-carbamoylpyridinium Chloride (*Ii*)

Procedure A: Solution of 0·1 mol 4-dimethylaminobenzonitrile[15] in 300 ml ether was added dropwise to solution of 0·15 mol lithium aluminium hydride in 300 ml ether with stirring and cooling with ice, and then the mixture formed was heated to boiling for 1 h. After cooling the reaction mixture was decomposed with 45 ml water and 15 ml 20% NaOH, the ether layer was separated, and the aqueous layer was washed with total 100 ml ether. The organic phases were combined and dried over potassium hydroxide, and the solvent was distilled off to give 7·5 g (50%) 4-dimethylaminobenzylamine (*IV*), b.p. 135°C/15 torr (ref.[16]: b.p. 158—159°C/25 torr). ^{1}H NMR spectrum: δ, ppm (CDCl₃, TMS): 2·83 s (CH₃N), 3·68 s (CH₂), 1·38 broadened s (NH₂) 6·92 A_2B_2 q (arom. H—C). Solution of 3·35 g amine *IV* in 50 ml absolute dioxane was added drop by drop to a stirred suspension of 6·5 g „Zincke salt"[12] *III* in 100 ml of the same solvent. The formed yellow solution gradually turned red whereupon yellow crystals of the quaternary salt *Ii* separated. After 12 h standing at room temperature with exclusion of air moisture the reaction product was collected by suction and washed subsequently with 10 ml absolute acetonitrile and 50 ml dry ether. Drying in vacuum gave 5·8 g (99%) compound *Ii* in the form of yellow crystals, m.p. 156—160°C (decomp.), strongly hygroscopic and readily decomposed by water. For $C_{15}H_{18}N_3OCl$ (291·8) calculated: 61·75% C, 6·22% H, 12·15% Cl, 14·40% N; found: 60·98% C, 6·36% H, 12·88% Cl, 14·40% N. ^{1}H NMR spectrum: δ, ppm (DMSO-d₆, TMS): 2·85 s (CH₃N), 5·74 s (CH₂), 7·06 A_2B_2 q (arom. H—C), 8·16 d (H—C₅, Py), 8·87 broadened s (NH₂), 8·98 d (H—C₄, Py), 9·26 d (H—C₆, Py), 9·76 s (H—C₂, Py).

Procedure B: Solution of 1·73 g benzoyl chloride in 30 ml absolute dioxane was added drop by drop to a solution of 2·2 g 4-dimethylamino-N,N-dimethylbenzylamine (*V*) (prepared according to refs[11,17]) in 30 ml of the same solvent. After separation of colourless crystals of reaction intermediate, the reaction mixture was made homogeneous by addition of 50 ml anhydrous

acetonitrile, whereupon a solution of 1·16 g nicotinamide *II* in 50 ml anhydrous dioxane was added drop by drop. The separated crystals (1·5 g) were filtered off, washed with anhydrous ether, and dried in vacuum. This procedure gave a non-uniform product, m.p. 167—168°C (decomp.), containing (according to ^{1}H NMR spectrum) the salt *Ii* together with another component exhibiting olefinic signals.

4-Dimethylaminobenzonitrile

The title substance was prepared by application of a recently described[18] synthetic method for preparation of aromatic nitriles: A mixture of 74·5 g 4-dimethylaminobenzaldehyde, 45 g hydroxylamine hydrochloride and 500 ml 99% HCOOH was heated to boiling for 45 min. After cooling, the reaction mixture was diluted with 500 ml water, and the solution formed was neutralized by addition of 5% NaOH solution. The precipitated crystals of product were collected by suction, and further portions were obtained by extraction of the filtrate with ether. After crystallization from methanol we obtained 25 g (34%) title nitrile, m.p. 74°C (ref.[9]: m.p. 76°C).

Electrochemical Experiments

The polarography was carried out with a three-electrodes arrangement using mercury dropping electrode as the indication electrode with platinum working electrode and saturated calomel reference electrode and the Radelkis OH 102 apparatus (Hungary). The measurements were carried out under inert atmosphere (nitrogen), the gas was dried with concentrated sulphuric acid and phosphorus pentoxide before use in the measurements in acetonitrile solutions. The cyclic voltammetry was measured with a GWP 673 Mehrzweck Polarograph (GDR) with platinum and hanging mercury dropping electrodes in water and in dimethylformamide.

The pH measurements of the solutions studied were carried out with a PAK 1 pH-meter (Czechoslovakia) with a glass electrode after each recording of the voltammetric curve. The following basic electrolytes were used: 0·05M-H_2SO_4 (pH 1·0), 0·2M acetate buffer (pH 4·8), Britton–Robinson buffer (pH 1·8 to 12). Constant ionic strength was adjusted by addition of $NaClO_4$ . .H_2O, the basic electrolyte for anhydrous acetonitrile being $(C_2H_5)_4N^+ClO_4^-$ salt. „Logarithmic analyses" of the polarographic curves were carried out with a Texas Instrument 9 calculator and the correlation curves were obtained by the least squares method using a Hewlett Packard 2916 B computer. In the case of the compound *Ii*, whose aqueous solutions are not stable, it was not possible to evaluate quantitatively the polarographic curves. For the correlation analyses the $E_{1/2}$ values from logarithmic analyses were used (Tables I—III).

RESULTS

The polarographic studies were carried out with solutions of the depolarizers in water, anhydrous acetonitrile and aqueous ethanol. The complete set of the quaternary salts *Ia—i* could only be investigated in acetonitrile without difficulties, since the dimethylamino derivative *Ii* is rapidly decomposed in the presence of water: $Ii + + 2 H_2O \rightarrow II + H_3O^+ + Cl^- + VI$. Due to this chemical transformation, only the quickly prepared solutions of the salt *Ii* in aqueous solvents give the expected cathodic waves, and the presence of amide *II* and amino alcohol *VI* can be proved

TABLE I

Electrochemical reduction of compounds *Ia—i* in aqueous solutions. Britton–Robinson buffer of pH 9·15, the depolarizer concentration $1 \cdot 10^{-3}$ mol l^{-1}

Compound		$I_d \cdot 10^6$, A			$-E_{1/2}$, V			$RT/\alpha nF$ mV[a]
	Wave *A*	*B*	*C*	*A*	*B*	*C*	
Ia	0·35	3·71	4·09	0·74	0·952	1·68	78
Ib	17·22[b]	3·90	max.	0·48[b]	0·957	1·72	80
Ic	0·19	3·01	max.	0·74	0·938	1·75	74
Id	—	3·52	max.	—	0·943	1·75	75
Ie[c]	0·37	2·08	4·61	0·71	0·932	1·73	74
If	0·38	3·79	4·21	0·74	0·947	1·70	69
Ig	0·35	4·54	4·45	0·72	0·972	1·67	80
h	0·45	4·06	4·13	0·75	0·970	1·71	74
Ii	*d*	*d*	max.	0·73	1·033	1·80	92

[a] The values calculated from logarithmic analysis of the polarographic waves *B*; [b] reduction of nitro group; [c] in addition the polarograms show one more wave at $-1·47$ V ($0·9 \cdot 10^{-6}$ A); [d] the values were not measured due to rapid decomposition of the depolarizer.

TABLE II

Electrochemical reduction of compounds *Ia—i* in anhydrous acetonitrile. Saturated solution of the depolarizer in anhydrous acetonitrile at 25°C; 0·075 mol l^{-1} $(C_2H_5)_4N^+ClO_4^-$

Compound	$-E_{1/2}$, V	$RT/\alpha nF$, mV[a]
Ia	0·998	69
Ib[b]	0·889	—
Ic	0·924	61
Id	0·926	70
Ie	0·959	67
If	0·986	66
Ig	1·016	68
Ih	0·976	71
Ii	1·033	69

[a] The values read from the logarithmic analyses; [b] reduction of nitro group proceeds in two further waves at $E_{1/2}$ $-1·16$ V and $-1·38$ V.

in the reaction medium by chromatography and polarography. The amide II shows (at pH 10·38) a reduction wave with $E_{1/2} = -1·76$ V and $\bar{I}_d = 7·8 \cdot 10^{-6}$ A which agrees with that of the standard sample.

Aqueous Solutions of Salts Ia—i

Table I gives a survey of the measured data. In solutions of pH 1 to 8 the polarograms show two waves, A and B. The third wave C does not appear until in mildly alkaline solutions (pH > 8). In solutions of pH above 11 the polarographic charactertistics are distorted due to decomposition of the depolarizers. The most positive wave A was characterized as an adsorption one, since its height and $E_{1/2}$ value are not changed with concentration, pH value, and position of reservoir. The wave B has diffusion character; its height is constant from pH 6 to 10, and the half-wave potential, too, does not vary from pH 5 to 12 in the case of the depolarizers Ia, $Ic—i$. According to expectation, a somewhat different polarogram is that of the nitro derivative Ib only. Instead of an adsorption pre-wave, it exhibits a four-electron reduction wave of nitro group, which corresponds to the known process[20]: $-NO_2 +$ $+ 4 e + 4 H^+ \rightarrow$ —NHOH $+ H_2O$, followed by usual waves B and C of the pyridine ring of the depolarizer.

TABLE III

Electrochemical reduction of compounds $Ia—i$ in 50% aqueous ethanol. Britton–Robinson buffer of pH 9·8, 50% v/v ethanol, ionic strength 0·15 ($NaClO_4.H_2O$), the depolarizer concentration $1 \cdot 10^{-3}$ mol l^{-1}

Compound	$\bar{I}_d \cdot 10^6$, A		$-E_{1/2}$, V		$RT/\alpha nF$, mV[a]
Ia	2·66		0·909		74
Ib[b]	5·54	max[c]	0·933	1·63[c]	54
Ic	2·17	4·45[c]	0·864	1·71[c]	76
Id	1·92		0·875		76
Ie	2·17		0·891		78
If	2·26		0·903		75
Ig	2·56		0·919		76
Ih	2·09		0·919		76
Ii	[d]		0·953		[d]

[a] The values read from logarithmic analyses of the polarographic wave B; [b] reduction of nitro group takes place at $-0·69$ V ($33·21 \cdot 10^{-6}$ A); [c] reduction wave C; [d] the values were not read due to rapid decomposition of the depolarizer.

Solutions of Salts Ia—i in Anhydrous Acetonitrile

Due to limited solubility of the depolarizers, the experiments were carried out with saturated solutions at 25°C without evaluation of the diffusion currents (Table II). Under these conditions, the compounds *Ia, Ic—i* only exhibit the characteristical wave *B* of diffusion nature besides a small pre-wave with $E_{1/2} = -0.7$ V corresponding to reduction of the oxygen present in the traces of moisture in the solvent (see similar cases in ref.[21]). Again a more complicated polarogram is that of the nitro derivative *Ib*, containing, besides the expected *B* wave with $E_{1/2} = -0.889$ V, two other waves with $E_{1/2} = -1.155$ V and -1.385 V which correspond obviously to two-step reduction of nitro group[20].

Solutions in Aqueous Ethanol

The polarograms of solutions of the compounds *Ia, Id—h* in 50% aqueous ethanol (Scheme in Fig. 1) show only the *B* wave which, in the case of the derivative *Ib*, is preceded by the above-mentioned wave of four-electron reduction of nitro group. The polarograms of *Ib* and *Ic* show the *C* wave even in this solvent. The compound *Ii* gives (besides the *B* wave) the reduction wave of nicotinamide *II* which is formed by the already mentioned decomposition of *Ii* (Table III). For the *B* wave it was found that in the pH range 1 to 6 (Britton–Robinson buffer) the limit diffusion current is decreased, and the $E_{1/2}$ value is shifted to more positive potentials. In the pH range 6 to 11 the both said characteristics are independent of the proton concentration, and the *B* wave is controlled by diffusion. The derivatives *Ia, Id—h* show a very weak wave at -1.65 V within pH range 8 to 8.5, but this wave disappears at still higher pH values.

The polarograms of solutions of *Ia* in 10 to 30% aqueous ethanol are similar to those of aqueous solutions (*A, B, C* waves), but increasing ethanol concentration brings about gradual disappearance of the *A* and *C* waves, the $E_{1/2}$ value of *B* wave being shifted to more positive potentials. Thus at the ethanol concentrations below
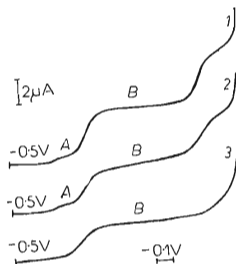

FIG. 1

Electrochemical reduction of compound *Ia* in solutions water–ethanol. Britton–Robinson buffer of pH 9·2, ionic strength 0·15 (NaClO₄. .H₂O), the depolarizer concentration $1 . 10^{-3}$ mol l⁻¹. *1* 0% EtOH; *2* 20% EtOH; *3* 50% EtOH

10% the alcohol effect is hardly perceptible, whereas at concentrations above 30% the reduction takes place in a single wave B (except for the compounds Ib and Ic). Addition of tert-butyl alcohol has similar effect as that of ethanol. *E.g.* at pH 9·15 at constant ionic strength $I = 0·15\ (NaClO_4.H_2O)$ (the depolarizer concentration $1 . 10^{-3}\ mol\ l^{-1}$) the compound Ia only shows the B wave at $E_{1/2} = -0·951$ V and $\bar{I}_d = 2·72 . 10^{-6}$ A (50% ethanol) and at $E_{1/2} = -0·955$ V and $\bar{I}_d = 2·82 .\ . 10^{-6}$ A (30% tert-butyl alcohol).
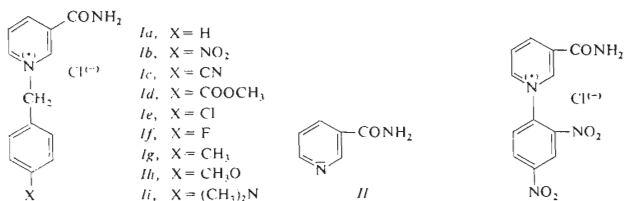
Cyclic Voltammetry

The said solutions of $Ia-h$ were submitted to a study at a platinum and a hanging mercury drop electrodes at the potential change rate $v \leq 100$ V s^{-1} at 25°C. In no case we could identify any unambiguous anodic peak corresponding to oxidation of a product formed by reduction at the B wave.

DISCUSSION

Mechanism of the Electrode Process

We tried to interpret the described polarographic behaviour of the salts $Ia-i$ by the mechanism given in Scheme 1 which was supported by convincing arguments[4,6,22,23] in the case of electroreductions of NAD^+ and its model compounds. The primary reaction step $VII \rightarrow VIII$ corresponds to the B wave, the subsequent step $VIII \rightarrow \rightarrow IX$ being ascribed to the C wave. Thus the mechanism E, E + C of the overall transformation $VII \rightarrow IX$ resembles very much in its character the oxidation of biological substrates with NAD^+ coenzyme, whose course in the presence of enzyme differs from Scheme 1 by reversibility of the last step only (*i.e.* $VII \rightleftharpoons IX$). This difference then results in overall reversibility $VII \rightleftharpoons IX$ with establishing of redox potential[24], whereby the enzyme system markedly differs electrochemically from the model systems. The alternative transformation 2 $VII \rightarrow X$ is completely suppressed in the case of biocatalysis, since fixation of the molecules VII and/or $VIII$ in the respective enzyme cavities[25] prevents migration of the reacting particles to bimolecular reaction 2 $VIII \rightarrow X$. Thus all the transformations given in Scheme 1 must be considered for our model substances $Ia-i$.

Although the reversibility of the first step $VII \rightarrow VIII$ was unambiguously proved for the substituents R = Me, Et, Pr, NMN^+ as well as for NAD^+ coenzyme[4,5,8,22,26,27], we tried to supply analogous evidence also in the cases of the depolarizers $Ia-i$. The results of logarithmic analyses of the polarographic curves for the B wave did not prove fully convincing, since the calculated values $RT/\alpha nF$ vary about 70 mV in accordance with a previous analogous finding[23] for the compound Ia. The results of the cyclic voltammetry carried out did not prove the said reversibility, either. We suppose, however, that our negative experimental findings
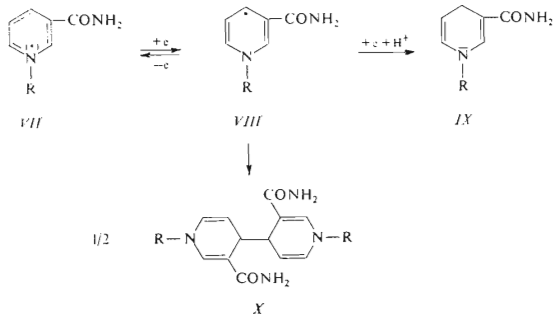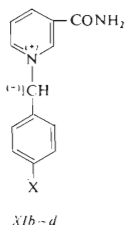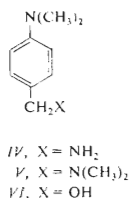
SCHEME 1

do not exclude the mentioned arguments[4,23] in favour of the discussed reversibility, because formation of the dimers *X* most likely diminishes accuracy of evaluation of the logarithmic analyses, and the cyclic voltametry could not be performed with such a rapid potential change as in ref.[5].

Interesting is the solvent effect on the polarographic behaviour in the individual reaction steps of Scheme 1 for the special case $R = p\text{-}XC_6H_4CH_2$, *i.e.* for our substances $Ia-i$. In the aqueous solutions the transformation $VII \rightarrow VIII$ always makes itself felt which is connected with general occurrence of the B wave. Formation of the C wave at pH 8 to 11 indicates that the corresponding proton concentration in the electrolyte is still sufficient also for realization of the subsequent transformation of radical $VIII$ into 1,4-dihydro derivative IX, which resembles the course of enzymatic reaction. At pH 8 the C wave is overlapped by decomposition of the
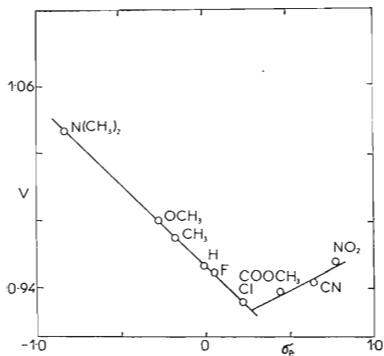

FIG. 2

Correlation between $E_{1/2}$ values of wave B of reduction of compounds I and σ_p values[33] — aqueous medium
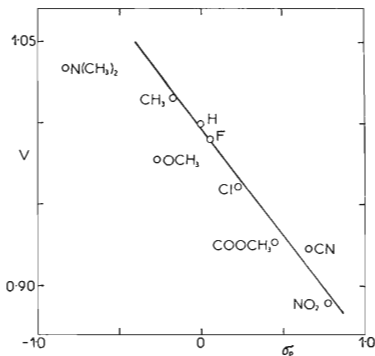

FIG. 3

Correlation between $E_{1/2}$ values of wave B of reduction of compounds I in anhydrous acetonitrile and σ_p values[33]

basic electrolyte and cannot be observed. An analogous effect can also be encountered with the compounds Ia and $Id - i$ even at higher pH values, if the ethanol concentration is higher than 30%, which has not yet been mentioned in literature. One of the possible decompositions of radical $VIII$ could consist in a reaction type $CH_3CH_2OH + 2\ VIII \rightarrow CH_3CHO + 2\ IX$ resembling the process catalyzed by alcohol dehydrogenases. A similar decomposition of the radical formed by reduction of N-alkyl-pyridinium salts *via* chemical reaction with another substrate was also observed[28]. However, the fact that the same effect is also exerted by tert-butyl alcohol indicates a possibility of secondary formation of other radical particles than those leading to formation of CH_3CHO. The following chemical processes can be considered to cause decomposition of radical $VIII$: $VIII + CH_3CH_2OH \rightarrow IX + CH_3\dot{C}HOH$, $2\ CH_3\dot{C}HOH \rightarrow CH_3CH(OH)CH(OH)CH_3$, $HO^- + CH_3\dot{C}HOH + I \rightarrow CH_3CHO + H_2O + IX$, $VIII + (CH_3)_3COH \rightarrow IX + (CH_3)_2C(OH)\dot{C}H_2$, *etc.* We consider it likely that an important role in the said effect can also be played by the alcoholate anion generated at higher pH values of medium by the reaction $C_2H_5OH + OH^- \rightleftharpoons \rightleftharpoons C_2H_5O^- + H_2O$ which transforms the starting depolarizer VII by known way[29] into the corresponding polarographically inactive tetramer or reacts with radical $VIII$ in a not yet known way. The former possibility is supported by the fact that height of the B wave is decreased by $1/3$ at pH 9·5 in 50% ethanol as compared with the corresponding situation in the absence of alcohol. On the contrary, the absence of the C wave for solutions of $Ia - i$ in anhydrous acetonitrile can be readily explained: the elementary step $VIII \rightarrow IX$ necessitates participation of the proton, and the solvent does not provide any. This phenomenon has already been observed[6] in similar cases.
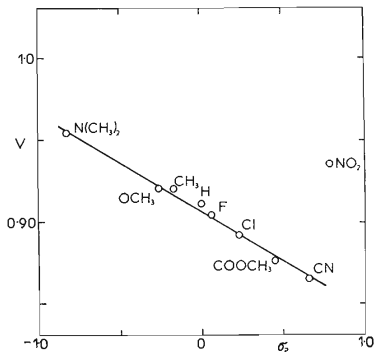

Fig. 4

Correlation between $E_{1/2}$ values of wave B of reduction of compounds I in 50% aqueous ethanol and σ_p values[33]

Substituent Effect

From Tables *I*—*III* it is seen that the substituents X cause the $E_{1/2}$ values of the *B* wave to vary by max. 0·14 V, the highest variability being in acetonitrile solutions. On the contrary, variation of the other waves is practically imperceptible (related to experimental error). The attempts of quantitative evaluation of substituent effect on the wave *B* use either the Hammett equation[30]

$$\Delta E_{1/2} \text{(solvent)} = \varrho_{pi,R}\sigma \tag{1}$$

or its two-parameter analogue

$$\Delta E_{1,2} \text{(solvent)} = \varrho_{pi,I}\sigma_I + \varrho_{pi,R}\sigma_R , \tag{2}$$

where the quantities σ, σ_I, and σ_R are the substituent constants published in ref.[31]. The results obtained with Eq. *(1)* are given in Figs 2—4. Obviously, in the case of $E_{1/2}(H_2O)$ the correlation field falls to two relations, one for *pi*-donor substituents $\left(X = OCH_3, N(CH_3)_2, CH_3, H, F, \text{and } Cl\right)$ having $\varrho_{pi,R} = +0.095$ V and the other for *pi*-acceptor substituents $(X = COOCH_3, CN, NO_2)$ having unusually negative value $\varrho_{pi,R} = -0.064$ V. An analogous decomposition of correlation (however, with opposite signs of $\varrho_{pi,R}$) was observed[32,33] in the case of polarographic reduction of *p*-substituted benzyl bromides and *p*-substituted benzenediazonium salts, and

TABLE IV
Characteristics of the correlation equations *(1)* and *(2)*

Medium	n^a	Equation *(1)*			Equation *(2)*		r	$S \cdot 10^3$
		$\varrho_{pi,R} \cdot 10$, V	r	$S \cdot 10^3$	$\varrho_{pi,I} \cdot 10$, V	$\varrho_{pi,R} \cdot 10$, V		
H_2O	6^b	0·95	0·993	4·51	1·15	0·93	0·999	0·04
	3^c	−0·64	0·864	8·59	^{d}	^{d}	—	—
CH_3CN	9	1·27	0·984	8·84	1·37	1·12	0·999	0·14
	7^e	0·87	0·923	1·95	1·22	0·65	0·999	0·29
50% C_2H_5OH	8^f	0·61	0·995	2·98	0·73	0·58	0·999	0·01

^{a} The number of the compared pairs; ^{b} for the substituents X = N(CH₃)₂, OCH₃, CH₃, H, F, Cl (Fig. 2); ^{c} for the substituents X = COOCH₃, CN, NO₂ (Fig. 2); ^{d} Eq. *(2)* was not investigated due to small number of experimental data; ^{e} not involved are the data for X = N(CH₃)₂ and OCH₃ (Fig. 3); ^{f} not involved is the date for X = NO₂ (Fig. 4).

it was interpreted[30] by a possibility of an alternative charge-transfer or bond-splitting mechanism of the electrode process. In our case the reversed effects of the both types of substituents X (Fig. 2) can be explained by formation of a C-ylide for the case $\sigma_p > 0$ by the reaction $I + OH^- \rightarrow XI + H_2O$. Formation of the ylide XIb from the nitro derivative Ib was observed by other authors[34]. The existence of negative charge at 1-substituent in ylide XI can explain the shift of $E_{1/2}$ values towards more negative values than those expected for quaternary salts $Ib-d$. The mentioned results indicate formation of the ylides $XIb-d$ which is here polarographically demonstrated. On the contrary, the $E_{1/2}(CH_3CN)$ values correlate with the expected positive value $\varrho_{pi,R} = +0.127$ V (Fig. 3) in accordance with the ylides $XIb-d$ being not formed in the absence of base. However, data for the compounds Ih and Ii with strong *pi*-donor groups X = $N(CH_3)_2$ and OCH_3 are distinctly deviated towards positive potentials (Fig. 3). Cause of these deviations can be hardly explained yet, it is, however, known[30] that data for the substituents OCH_3 and $N(CH_3)_2$ are often deviated from the correlation straight lines (Eq. (1)) for various solvents. In this respect it is noteworthy that the $E_{1/2}$ (50% C_2H_5OH) and $E_{1/2}$ (H_2O) values do not show such deviations (Figs 2 and 4). Furthermore, from Fig. 4 it is seen that relatively the closest linear correlation (1) for all the substituents X (except for NO_2) is obtained in aqueous ethanol. The said exception (NO_2) can be explained most easily by formation of the ylide XIb. The fact that the points for the substituents X = $COOCH_3$ and CN do not deviate (in contrast to the $E_{1/2}$ (H_2O) values; *cf.* Figs 2 and 4) indicates that addition of alcohol suppresses formation of the ylides XIc,d.

TABLE V
Comparison of the calculated values with the experimental ones. Solutions of compounds $Ia-g$ in anhydrous acetonitrile. All the data are given in Volts

Compound	$-E_{1/2,\text{calc.}}$[a]	$\Delta E_{1/2} \cdot 10^{2b}$	$-E_{1/2\text{calc.}}$[c]	$\Delta E_{1/2} \cdot 10^{2b}$
Ia	0·993	−0·45	0·994	−0·30
Ib	0·893	0·49	0·888	−0·08
Ic	0·909	−1·47	0·911	−1·25
Id	0·936	1·0	0·943	1·76
Ie	0·964	0·51	0·964	0·53
If	0·986	−0·02	0·984	−0·17
Ig	1·015	−0·08	1·011	−0·49

[a] Calculated from Eq. (1); [b] $E_{1/2,\text{calc.}} - E_{1/2,\text{exp}}$ (Table II); [c] calculated from Eq. (2).

The results of correlation analysis by the two-parameter equation (2) are given in Table IV. If the above-mentioned division of the correlation field is respected, then the relations (1) are obviously relatively close. Introduction of the two-parameter correlation (2) improves quality of statistical criteria in all the cases and, at the same time, indicates that in water solutions the formal inductive effect (represented by the $\varrho_{pi,I}$ parameter) is slightly more significant than the resonance component (represented by the $\varrho_{pi,R}$ parameter). However, physical meaning of the correlation (2), as compared with that of (1), is not convincing. This statement is supported by comparison of deviation between the experimentally measured half-wave potentials and the $E_{1/2}$ values calculated under the assumption of validity of relation (2). From Table V it is seen that agreement between the calculated and the found $E_{1/2}$ values is worse with the correlation (2) than that with (1), even though the latter shows statistical characteristics of lower quality (Table IV). It is also noteworthy that the correlation (2) cannot remove the partial non-homogeneity of the correlation field in Figs 3 and 4.

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