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POLAROGRAPHIC STUDY OF N-PHENYLBENZIMIDAZOLIUM, N-PHENYLPERIMIDINIUM, AND NAPHTH[2,3-d]IMIDAZOLIUM IONS

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The effect of the N-phenyl group on the ease and character of the polarographic reduction of benzimidazolium and perimidinium ions was studied. The effect of the introduction of a phenyl group in the 1 position of the benzimidazolium cation is approximately equal to the effect of a benzene ring condensed in the 5 and 6 positions and considerably exceeds the effect of a phenyl group introduced in the 2 position and of a benzene ring condensed in the 4 and 5 positions.

It is known that the N-phenyl group in series of five-membered nitrogen heterocycles has an appreciable effect on the physical and chemical properties of compounds [1]; in particular, it facilitates the reduction of the heteroring in 1-phenylindole [2] and changes the character of the reaction with nucleophiles in the case of 1-arylbenzimidazoles [3,4] and their quaternary salts [5]. Considering that the free electron is the simplest nucleophile, we studied the polarographic reduction of N-phenylbenzimidazolium (I and II) and N-phenylperimidinium (V) salts in comparison with the reduction of the previously studied [6] 1,3-dimethylbenzimidazolium (III) and 1,3-dimethylperimidinium (VI) salts. In addition, it was important to compare the effect on the ease of addition of electrons of, on the one hand, the N-phenyl group in the cations of I, II, and V and, on the other, the 2-phenyl group in the 1,3-dimethyl-2-phenylbenzimidazolium cation (IV) and of the condensed benzene ring in the cations of linear (VII) and angular (VIII) naphthimidazoles (see scheme).

Because of the limited solubility of the investigated compounds in water, the reduction was carried out in aqueous dimethylformamide (DMF) containing 10% (by volume) DMF. Tetraethylammonium perchlorate was used as the inert electrolyte; buffer solutions were not used because of hydrogen evolution, since this process masks the reduction wave of the investigated ions. The reduction potentials obtained and the literature values for the cations of III, IV, VI, and VIII are presented in Table 1.

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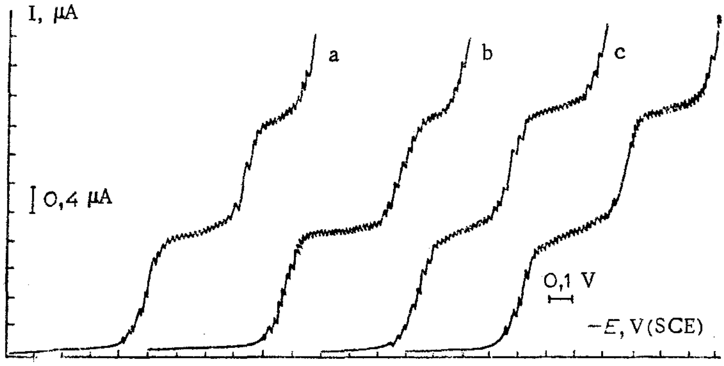


Fig. 1. Polarograms of the investigated salts in 0.1 N $(C_2H_5)_4NClO_4$: a) 1-phenyl-3-methylbenzimidazolium perchlorate (I); b) 1-(p-anisyl)-3-methylbenzimidazolium perchlorate (II); c) 1-phenyl-3-methylperimidinium perchlorate (V); d) 1,3-dimethylnaphth[2,3-d]-imidazolium perchlorate (VII).

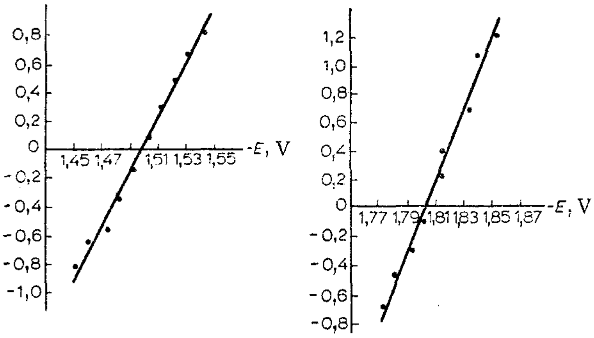
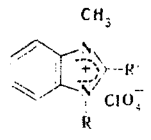


Fig. 2. Dependence of log $[i^{2/3}/(i_d - i)]$ on E for the first wave (a) and dependence of log $[i^{3/2}/(i_d - i)]$ on E for the second wave (b) on the polarograms of 1-phenyl-3-methylbenzimidazolium perchlorate (I).

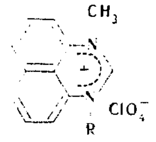
TABLE 1. Half-Wave Potentials of the Polarographic Reduction of Benzimidazolium and Perimidinium Cations

Compound	$-E_{1/2}$, V		Note
	first wave	second wave	
I	1,50	1,81	Two one-electron waves
II	1,50	1,86	" "
III[6]	1,85	—	One two-electron wave
IV[7]	1,78	—	" "
V	1,35	1,68	Two one-electron waves
VI[5]	1,42	1,78	" "
VII	1,42	1,76	" "
VIII[5]	1,75	—	One two-electron wave

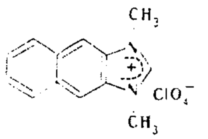
The reduction of benzimidazolium perchlorate I proceeds with two waves with approximately equal heights and half-wave potentials $E_{1/2} = -1.5 \pm 0.01$ V and $E_{1/2} = -1.81 \pm 0.01$ V, respectively (Fig. 1a). Analysis showed that the limiting currents of these waves are diffusion-controlled. Thus at concentrations ranging from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-4}$ mole/liter the limiting current is directly proportional to the depolarizer concentration; in addition, a directly proportional dependence between the limiting current and the square root of the height of the mercury column is also observed. Electrolysis at a controllable potential of the first



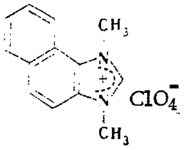
I–IV



V, VI



VII



VIII

I $R=C_6H_5$; $R'=H$; II $R=p\text{-}CH_3OC_6H_4$; $R'=H$; III $R=CH_3$; $R'=H$; IV $R=CH_3$; $R'=C_6H_5$;
V $R=C_6H_5$; VI $R=CH_3$

and second waves showed that each of the waves corresponds to a process with the addition of one electron. It may be assumed that the first wave is associated with the formation of a free radical, which subsequently reacts with mercury or undergoes dimerization to give products of the R–Hg–R or R–R type. It is known [8] that the form of the wave for processes of this sort is described by the equation

$$E=\varepsilon_0-\frac{RT}{nF}\ln\frac{i^{2/3}}{i_d-i},$$

in which case the graph of the wave in coordinates of log $[i^{2/3}/(i_d-i)]$ and E should be expressed by a straight line with a reciprocal slope of about 59 mV. Logarithmic analysis of the first wave of the cation of I showed that the wave is rectified in the indicated coordinates (Fig. 2a); this confirms a reduction mechanism in which a bimolecular chemical reaction follows the electrochemical reaction.

The second wave on the polarograms of the cation of I corresponds to reduction of the free radicals to 1-phenyl-3-methyl-2,3-dihydrobenzimidazole (the reduction of benzimidazolium salts by means of potassium borohydride proceeds similarly [9]). A bimolecular chemical reaction also takes place in addition to reduction of the radicals. In fact, the second wave of I (Fig. 2b) is also rectified in coordinates of log $[i^{3/2}/(i_{lim}-i)]$ and E.

The reduction of benzimidazolium perchlorate II proceeds completely analogously (Fig. 1b). It should only be noted that whereas the first wave of the cation of II is found at the same potential as that observed for the cation of I, the second wave is shifted slightly to the more negative region. The chemical data also indicate that the p-methoxy group in 1-(p-anisyl)benzimidazole increases the electron density in the imidazole ring slightly [10].

The most interesting feature of the polarographic behavior of N-arylbenzimidazolium salts is their difference from the cations of III and IV, which are reduced in one two-electron wave with $E_{1/2}$ = −1.85 and −1.78 V, respectively. This constitutes evidence that an N-phenyl group substantially facilitates the addition of the first electron and stabilizes the intermediately formed free radical to a greater degree than in the case of the 2-phenyl substituent. This conclusion also holds for series of perimidinium cations, in which perimidinium cation (V) is reduced in two one-electron diffusion steps with $E_{1/2}$ = −1.35 ± 0.01 V and $E_{1/2}$ = −1.68 ± 0.01 V (Fig. 1c), whereas the 1,3-dimethyl-2-phenylperimidinium cation is reduced in one two-electron step with E = −1.38 V [6]. However, one's attention is directed to the fact that a phenyl substituent in the 2 position in the perimidinium system facilitates reduction to a considerably smaller extent than it does in the benzimidazolium cation. Another difference between perimidinium and benzimidazolium cations is the fact that the character of the reduction (two one-electron waves) does not change on passing from the 1,3-dimethylperimidinium cation to the 1-phenyl-3-methylperimidinium cation; only the electrophilicity of the cation increases somewhat. The cation of V is the most electrophilic of all of the cations of the salts investigated in the present research.

The reduction of imidazolium perchlorate VII proceeds in two one-electron diffusion steps with half-wave potentials $E_{1/2}$ = −1.42 and −1.76 V (Fig. 1d). It was concluded that these waves and the mechanism have diffusion character on the basis of studies similar to those made for I (as well as II and V). The cation of VII is virtually identical to the I cation of I with respect to the ease and character of reduction and differs markedly from the imidazolium cation of VIII, which is reduced in one two-electron wave and, moreover, with considerably greater difficulty ($E_{1/2}$ = −1.75 V).

Thus our research demonstrated that the N-phenyl group substantially facilitates the polarographic reduction of N-heteroaromatic cations and in some cases even changes the character of the process. If the 1,3-dimethylbenzimidazolium cation is taken as the standard, the effect of the introduction of a N-phenyl substituent is equal to the effect of a benzene ring condensed in the 5 and 6 positions (the cation of VII) and considerably exceeds the effect of a 2-phenyl substituent and a benzene ring condensed in the 4 and 5 positions (the cations of IV and VIII).

EXPERIMENTAL

The studies were carried out with LP-7 and PPT-1 polarographs at 22 ± 0.5°C with Kalousek and three-electrode cells. A dropping mercury electrode with the following characteristics served as the polarizable electrode: $t = 4.0$ sec and $m = 2.90$ mg/sec (in a 0.1 N KCl solution at a mercury column height of 30 cm with an open circuit). In the measurements with the Kalousek cell the polarizing comparison electrode was a saturated calomel electrode (SCE) ($\varphi = +0.241$ V), the potential of which was checked periodically by recording the polarograms of Tl_2SO_4 solutions and by comparison of the half-wave potential of the Tl^+ ion thus obtained with the tabular value. The three-electrode cell was used in the experiments for the determination of the half-wave potentials. The potential of the dropping mercury electrode relative to an aqueous saturated calomel electrode was measured by means of a digital dc voltmeter of the Shch-1413 type (the initial resistance was 100 MΩ). All of the potentials are given relative to the saturated calomel electrode. A cell with a large mercury cathode and cathode and anode spaces separated by a porous diaphragm was used for the coulometric measurement of the number of electrons that participate in the reduction; the auxiliary electrode was prepared from smooth platinum.

1-Phenyl-3-methyl-benzimidazolium Iodide. This compound was obtained as colorless crystals, with mp 195°C (from alcohol), by refluxing a mixture of 1.94 g (0.01 mole) of 1-phenylbenzimidazole, 3 ml of methyl iodide, and 20 ml of acetone for 2 h.

1-Phenyl-3-methylbenzimidazolium Perchlorate (I). This compound was obtained as colorless crystals, with mp 164°C (from alcohol), by mixing aqueous solutions of iodide I and sodium perchlorate.

The other salts were obtained by similar methods.

1-(p-Anisyl)-3-methylbenzimidazolium Iodide. This compound was obtained as colorless crystals with mp 203°C (from alcohol). 1-(p-Anisyl)-3-methylbenzimidazolium perchlorate (II) was obtained from it in the form of colorless crystals with mp 190°C (from alcohol).

1-Phenyl-3-methylperimidinium Iodide. This compound was obtained as yellow crystals with mp 253°C (dec., from alcohol with water). Perchlorate V was obtained from it in the form of colorless crystals with mp 265°C (dec., from alcohol).

Perchlorates III, IV, VI, and VIII and the corresponding iodides were described in [6].

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