

IV.* ROLE OF ONE-ELECTRON TRANSFER IN REACTIONS WITH ARYLAMINES

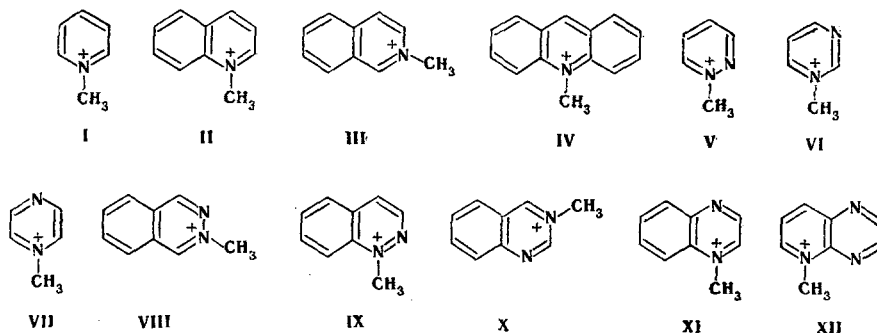
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A satisfactory correlation between the polarographic reduction potentials and the calculated energies of the lower vacant molecular orbitals was found for a number of N-methylazinium cations. The result of the aza effect and the benzoannellation effect is a shift of the reduction potentials to the positive region by 0.2-0.5 and 0.2-0.7 V, respectively. Electron transfer from N,N,N',N'-tetramethyl-p-phenylenediamine to the most electrophilic cations was recorded. The possibility of the occurrence of reactions involving aminoarylation of the acridinium cation via a one-electron mechanism was demonstrated electrochemically and by model reactions.

Nucleophilic substitution of hydrogen in heteroaromatic compounds always occurs with the participation of partners with pronounced donor-acceptor properties, and this suggests the possibility of the occurrence of such reactions via a one-electron mechanism [2].

The aim of the present research was to investigate the possibility of electron transfer processes in the reactions of azinium cations with uncharged aromatic nucleophiles. In addition, we proposed to obtain a quantitative evaluation of the structural changes introduced by the aza grouping and annellation of the benzene ring.



Electrochemical modeling of nucleophilic attack with the participation of azinium cations with the following successively changing structures was carried out in this research: 1-methylpyridinium (I), 1-methylquinolinium (II), 2-methylisoquinolinium (III), 10-methylacridinium (IV), 1-methylpyridazinium (V), 1-methylpyrimidinium (VI), 1-methylpyrazinium (VII), 2-methylphthalazinium (VIII), 1-methylcinnolinium (IX), 3-methylquinazolinium (X), 1-methylquinoxalinium (XI), and 5-methylpyridinio[2,3-b]pyrazine (XII). The perchlorates of cations I-IX, XI, and XII were reduced on a dropping mercury electrode; because of the inaccessibility of the perchlorate of X, its iodide was used.†

*See [1] for communication III.

†The $E_{1/2}$ values for the iodides differ by 20-40 mV from the corresponding values for the perchlorates [3].

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TABLE 1. Polarographic Reduction Potentials of Methylazinium Salts on a Dropping Mercury Electrode in DMF with a 0.1 N Bu₄NClO₄ Base Electrolyte Relative to a Saturated Calomel Electrode and Calculated Energies of the Lower Antibonding Orbitals (lao)

Compound ^a	$-E'_{1/2}$, V	$\Delta E'$, mV ^b	i'' , μ A	$-E_{lao}$, β units
I	1.269	43	2.5	0.507
II	0.842	47	2.0	0.317
III	1.046	47	1.9	0.404
IV ^c	0.319	63	1.9	0.169
V	0.741	48	2.4	0.397
VI	0.938	46	1.9	0.497
VII	0.728	53	2.4	0.381
VIII	0.861	49	2.4	0.390
IX ^d	0.533	56	2.0	0.206
X	0.327	65	2.0	0.375
XI	0.368	53	2.4	0.195
XII	0.344	54	2.2	0.241
XIII ^e	2.823	73	3.2	—

a) All of the waves are one-electron waves. b) These are the slopes on the graphs in semilogarithmic coordinates $E/\ln(i^{2/3}/i_d - i)$. c) Characteristics of the second wave: $E_{1/2}'' = -2.790$, $E'' = 77$, $i'' = 1.7$. d) For the reversible wave. All of the remaining waves are irreversible and correspond to dimerization. e) One two-electron wave.

The results of the polarographic investigations presented in Table 1, which we obtained under identical conditions for all of the cations, are in complete agreement with the data in [4] on the reduction of cations I and II. The reduction of diazonium cations V-VII has also been described [5]. However, their reduction potentials were determined by a different method in [4], and the reduction potentials of the iodides were determined in [5].

Two waves are observed on the polarograms of all of the compounds. The first wave is a one-electron wave. The number of electrons was determined by the method in [6]. Construction of the graph in the semilogarithmic coordinates $E/\ln(i^{2/3}/i_d - i)$ shows that electron transfer is accompanied by dimerization of the resulting radicals [7]. The second two-electron wave probably corresponds to subsequent steps in the reduction of the resulting radicals and dimers. This was demonstrated by polarographic reduction of XIII, obtained by a chemical method (Table 1). A one-electron mechanism for the reduction of cations I-IV and their derivatives with subsequent dimerization was also demonstrated in [8, 9].

Comparison of the reduction potentials in the pyridinium-quinolinium, isoquinolinium-acridinium series shows that annelation of the benzene ring leads to a shift of the potential of the first wave to the positive region by 0.2-0.5 V. The same potential shift is also observed on passing from diazinium cations to benzodiazinium cations, except for the N-methylphthalazinium ion, which is reduced at a somewhat more negative potential as compared with the N-methylpyridazinium ion.

The effect of the aza group can be estimated by comparing the reduction potentials of the diazinium cations with that of the pyridinium ion and the reduction potentials of benzo-diazinium cations with those of the quinolinium and isoquinolinium ions. In all cases the aza group increases the electron-acceptor character, and the potential shift ranges from 0.2 to 0.7 V.

Thus both the aza group and the benzene ring increase the electron affinity, but the magnitude of their effect is different in each case and is determined by the relative orientation of the nitrogen atoms and the orientation of the benzene ring.

The results of the polarographic studies were compared with the results of quantum-chemical calculation by the MO LCAO method within the Hückel approximation. The correlation relationship between the reduction potentials and the calculated energies of the lower antibonding orbitals (E_{lao}) is shown in Fig. 1. The trend of the change in the $E'_{1/2}$ values in the series of azinium cations is the same as the trend in the changes in the E_{lao} values. Good correlation of their values is observed in a structurally more related series of azinium

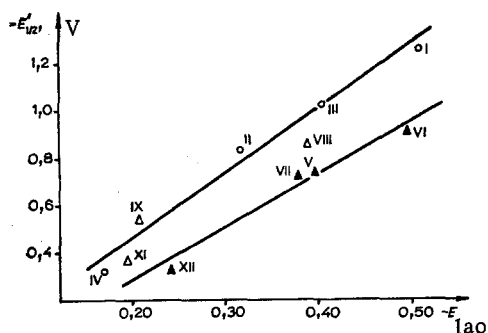


Fig. 1. Correlation relationship between the reduction potentials and the calculated energies of the lower antibonding orbitals (E_{1ao}).

cations, for example in the series of monoazinium cations I-IV ($r = 0.98$) and in the series of diazinium cations V-VII and XII ($r = 0.96$) (Fig. 1).

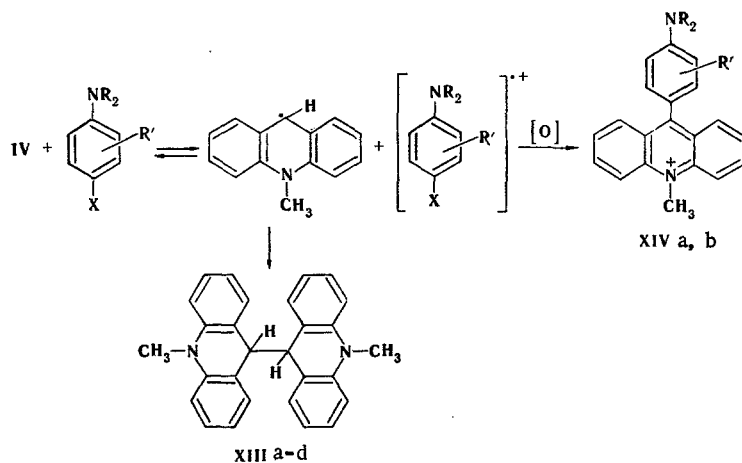
The one-electron reduction of cations I-XII as a model of their reactions with nucleophiles and the correlation of the potentials of the first step of the reduction with the energies of the lower vacant orbitals provide evidence for the possibility of the occurrence of these reactions via a one-electron mechanism [10].

The data from chemical studies carried out with cation IV confirm this conclusion. Thus it has been previously shown that a charge-transfer complex (CTC) is formed when solutions of N-methylacridinium iodide and dimethylaniline are mixed [11]. In the present research it was established that dimerization of the acridine ring is observed in the reaction of IV iodide with N,N-dimethyl-p-toluidine and N,N-dimethyl-p-anisidine, i.e., with arylamines in which the reaction centers (the para and ortho carbon atoms) are blocked. A dimer is also formed in the reaction of the acridinium cation with p-phenylenediamine, whereas the usual products of nucleophilic substitution (XIV) are formed with o- and m-phenylenediamines [12]. Since the tendencies of the isomeric phenylenediamines to transfer an electron are approximately identical, as evidenced by the closeness of their ionization potentials [13], it may be assumed that the occurrence of the reaction via the first or second pathway is associated with the stability of the particles that develop under electron transfer. It is known that, in contrast to p-phenylenediamine, the ortho and meta isomers do not give stable cation radicals when they are oxidized [14].

Electron transfer can be recorded if N,N'-tetramethyl-p-phenylenediamine (XV) is used as the donor. Thus a mixture of IV perchlorate and XV in DMF gives the characteristic "Wurster's Blue" coloration, whereas an intense signal of the cation radical of XV, identical to that described in [15], is observed in the ESR spectrum of the reaction solution. Dimer XIII was obtained in the preparative reaction of cation IV with XV.

The facts set forth above are in agreement with the reaction scheme depicted below.

The tendency to add one electron is also peculiar to other N-methylazinium cations. The spectrum of the cation radical of amine XV is also recorded in the reaction with cations X-XII.



XIII a $R=CH_3$, $R'=H$, $X=N(CH_3)_2$; b $R=CH_3$, $R'=H$, $X=CH_3$; c $R=CH$, $R'=H$, $X=OCH_3$;
d $R=H$, $R'=H$, $X=NH_2$; XIV a $R=H$, $R'=NH_2(o)$, $X=H$; b $R=H$, $R'=NH_2(m)$, $X=H$

TABLE 2. N-Methylazinium Perchlorates

Compound	mp, °C	Found, %			Empirical formula	Calc., %		
		C	H	N		C	H	N
I	136—137	37.4	4.2	7.3	C ₆ H ₈ NCIO ₄	37.2	4.2	7.2
II	120—121	49.5	4.1	5.6	C ₁₀ H ₁₀ NCIO ₄	49.3	4.1	5.7
III	117—118	49.6	4.4	5.4	C ₁₀ H ₁₀ NCIO ₄	49.3	4.1	5.7
IV	240—242	57.5	4.1	4.6	C ₁₄ H ₁₂ NCIO ₄	57.2	4.1	4.8
V	142—143	31.1	3.7	14.6	C ₅ H ₇ N ₂ ClO ₄	30.9	3.6	14.4
VI	65	31.1	3.7	—	C ₅ H ₇ N ₂ ClO ₄	30.9	3.6	—
VII	69	30.6	3.9	14.6	C ₅ H ₇ N ₂ ClO ₄	30.9	3.6	14.4
VIII	169—170	44.2	3.8	11.6	C ₉ H ₉ N ₂ ClO ₄	44.2	3.7	11.4
IX	153—154	44.3	3.7	11.4	C ₉ H ₉ N ₂ ClO ₄	44.2	3.7	11.4
XI	162—164	44.0	3.8	11.4	C ₉ H ₉ N ₂ ClO ₄	44.2	3.7	11.4
XII	164—165	38.9	3.4	17.2	C ₈ H ₈ N ₃ ClO ₄	39.1	3.3	17.1

It should be noted that the reaction of azinium cations with XV may serve as a unique test for the qualitative evaluation of their electrophilicity. When the components are mixed in DMF solution, the most electrophilic cations IV and IX-XII (Table 1) immediately give the characteristic blue color of the cation radical of arylamine XV. The remaining cations form solutions with colors ranging from yellow to red, apparently due to the formation of a CTC.

EXPERIMENTAL

The polarograms were recorded with an LP-7 polarograph at 20°. The dropping mercury electrode had the following characteristics: $m = 1.55$ mg/sec, $\tau = 0.2$ sec, and $U = -1.0$ V. The reversibility of the waves was determined by means of a Kalousek switch at 50 Hz. The ESR spectra of DMF solutions were recorded with a Rubin radiometer at 20°. The concentration of the components was 10^{-3} mole/liter. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The quantum-chemical calculations were performed by means of the Hückel D program with Pullman parameters [16].

The nitrogen bases and their methiodides were synthesized by the following methods: pyridazine [17], pyrimidine [18, 19], pyrazine [20, 21], cinnoline [22], phthalazine [23], quinazoline [24], quinoxaline [25], and pyrido[2,3-b]pyrazine [26, 27]. The methiodides of pyridine, quinoline, isoquinoline, and acridine were obtained from the commercial-grade bases.

Perchlorates of Cations I-IX, XI, and XII. These salts were synthesized from the corresponding iodides by exchange with copper perchlorate. A 10-mmole sample of the appropriate iodide was dissolved by heating in the minimum amount of ethanol, and a solution of 1.6 g (6 mmole) of copper perchlorate in 3 ml of water was added. The precipitated CuI₂ was removed by filtration and crystallized from ethanol. The purity of the compounds was verified by the results of elementary analysis (Table 2).

Reaction of IV Iodide with N,N-Dimethyl-p-toluidine. A mixture of 1.6 g (5 mmole) of IV, 1 ml (7 mmole) of amine, and 6 ml of DMSO was maintained in an argon atmosphere at room temperature for 30 days, after which the precipitated N,N'-dimethyldiacridanyl was removed by filtration and crystallized from DMF to give 0.2 g (20%) of colorless needles with mp 280-281°. No melting-point depression was observed for a mixture of a sample of this product with a sample obtained by the method in [28]; the two samples also had identical IR spectra.

The reaction of cation IV with N,N-dimethyl-p-anisidine proceeds similarly. The yield of dimer XIII was 0.17 g (17%).

Reaction of the Acridinium Cation with N,N'-Tetramethyl-p-phenylenediamine. The reaction was carried out with 1 g (3 mmole) of IV iodide, 0.6 g (4 mmole) of XV, and 3 ml of DMSO in an argon atmosphere at room temperature for 7 days. The precipitated N,N'-dimethyldiacridanyl was removed by filtration and crystallized from DMF to give 0.27 g (45%) of a product with mp 280-281°.

The yield of dimer XIII was 0.22 g (37%) in the reaction of IV iodide with p-phenylenediamine under the same conditions.

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