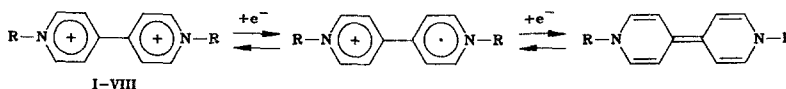


I. P. Krainov, S. F. Kramarenko,  
E. I. Dotsenko, A. A. Bumber,  
E. S. Klimov, and O. Yu. Okhlobystin

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The N,N'-aryl substituted bipyridinium perchlorates were studied by the methods of cyclic voltamperometry and classical and commutated polarography in DMFA. It was shown that cation-radicals, which are stable in an atmosphere of argon, are formed at the first stage of reduction. The reversibility and the number of the subsequent stages depend on the nature of the substituent at the nitrogen atom. The formation of the bipyridinium cation-radicals was confirmed by the method of EPR spectroscopy.

Bipyridinium salts (viologens) find application in the production of electrooptical devices as the reversible component of spectroelectrooptical cells [1]. These organic salts can exist in three oxidation-reduction states [2].



I-VIII  
I R=C<sub>6</sub>H<sub>4</sub>-OCH<sub>3</sub>; II R=C<sub>6</sub>H<sub>4</sub>-CN; III R=CH<sub>3</sub>; IV R=C<sub>6</sub>H<sub>4</sub>Cl; V R=C<sub>6</sub>H<sub>4</sub>-CO-OCH<sub>3</sub>;  
VI R=C<sub>6</sub>H<sub>5</sub>; VII R=CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>; VIII R=C<sub>6</sub>H<sub>4</sub>Br

The object of the present work was the study of the reduction of viologens, the majority of which have not previously been investigated, by the methods of classical and commutated polarography, cyclic voltamperometry (CVA), and EPR spectroscopy.

The reduction of the compounds (I)-(VIII) (Table 1) proceeds in two single-electron stages by the scheme presented above. The presence of the commutated polarograms with the potentials  $E_{1/2}$  close to the classical values testifies to the reversibility of the processes in the first stage for all compounds.

The method of CVA confirms the results obtained on the platinum electrode (Table 2) and indicates the relatively high stability of the cation-radicals formed.

The second stage of the reduction is not reversible in all cases. The corresponding cathodic peak is quasi-reversible for compound (I); it is completely irreversible for compound (V). Consequently, the reduced uncharged forms of (I) and (V) are unstable (Fig. 1).

The benzylviologen (VII) is reduced in four stages, the first two of which are reversible and single-electron, in contrast to the behavior of the compounds described. The third and fourth stages of the reduction are almost completely irreversible (Fig. 1); this is probably on account of the rapid ensuing reactions involving the participation of the products of the electrochemical reactions.

The reversibility of the first stage of the reduction of all of the viologens studied shows little dependence on the presence of oxygen in the DMFA. This is expressed by the fact that the values of the limiting currents of the commutated polarograms are practically unchanged in the presence of oxygen in the air (Table 1). Consequently, the rate of the interaction of the bipyridinium cation-radicals with oxygen cannot be high.

The existence of cation-radicals of the viologens studied was confirmed by EPR spectroscopy. The reduction of the benzylviologen (VII) on a zinc surface in DMF leads to the formation of the EPR spectrum of the cation-radical (Fig. 2). The central portion of the spectrum

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TABLE 1. Polarographic Behavior of the Bipyridinium Perchlorates (I)-(VIII) ( $E_{1/2}$  is the half-wave potential, V;  $i$  is the wave height,  $\mu\text{A}$ ;  $i'$  is the height of the commutated wave in the presence of oxygen in the air)

Compound	Classical polarography		Commutated polarography		
	$-E_{1/2}$	$i$	$-E_{1/2}$	$i$	$i'$
I	0,25	0,89	—	0,44	0,34
	0,56	1,00	0,60	0,40	—
II	0,16	0,78	0,23	0,39	0,40
	0,34	0,97	0,38	0,31	—
III	0,47	1,0	0,50	0,46	0,38
	0,80	0,90	0,82	0,40	—
IV	0,23	0,92	0,28	0,42	0,37
	0,50	1,02	0,56	0,40	—
V*	0,14	0,86	0,18	0,45	0,40
	0,35	0,91	—	—	—
VI	0,23	0,88	0,25	0,43	0,39
	0,44	1,05	0,46	0,41	—
VII	0,26	0,80	0,28	0,52	0,40
	0,53	0,75	0,60	0,40	—
	0,95	2,0	—	—	—
	1,29	4,2	—	—	—
VIII	0,18	0,81	0,22	0,38	0,30
	0,44	1,0	0,54	0,35	—

\*A third wave of reduction is observed with the maximum at  $E_{1/2} = -0.95$  V.

TABLE 2. Characteristics of the Cyclic Voltamperograms of the Bipyridinium Perchlorates (I)-(VIII) on a Platinum Disk Electrode ( $E_p$  is the potential of the peak, V;  $i$  is the height of the peak,  $\mu\text{A}$ )

Compound	Reduction		Oxidation	
	$-E_p$	$i$	$-E_p$	$i$
I	0,39	8,8	0,25	8,6
	0,73	8,8	0,55	6,0
II	0,22	8,6	0,16	8,5
	0,40	8,0	0,34	8,2
III	0,51	9,0	0,48	9,2
	0,90	8,8	0,87	8,8
IV	0,30	10,2	0,26	10,0
	0,50	9,1	0,53	9,1
V	0,26	7,6	0,20	7,8
	0,42	7,7	—	—
VI	0,24	9,0	0,18	9,4
	0,50	9,0	0,45	9,0
VII	0,37	9,0	0,33	9,0
	0,65	9,0	0,60	8,0
	1,14	15,0	—	—
	1,80	18,0	—	—
VIII	0,24	8,5	0,19	8,4
	0,52	8,5	0,42	8,3

is shown in Fig. 2 (the outer components are not visible in the conditions of the scanning). The hyperfine structure of this spectrum is practically the same as those obtained for the bipyridinium cation-radicals previously. The changes in the values of the splitting constants in the same solvent on varying the substituents at the nitrogen atoms are not sharply characterized; the multiplicity factor of the constants of the hyperfine splitting is a characteristic feature of the EPR spectra in many cases [3-6]. It follows from the EPR spectrum that the unpaired electron is delocalized over the entire cation-radical skeleton of the bipyridin-

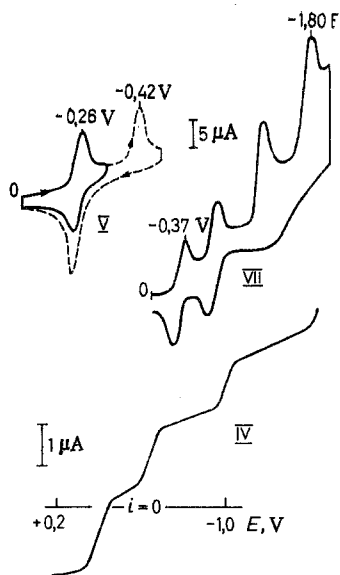


Fig. 1

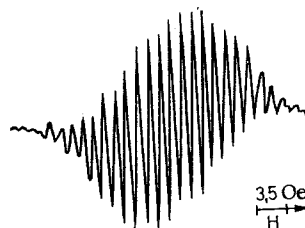


Fig. 2

Fig. 1. The cyclic voltamperogram of the compounds (V) and (VII) and the polarogram of compound (IV) obtained after the electrolysis at a controlled potential.

Fig. 2. The EPR spectrum of the cation-radical of the benzylviologen (VII) in DMF at 25°C.

ium fragment and over the benzyl substituents at a nitrogen atom. The hyperfine structure of the spectrum is determined by the interaction of the energy levels of the unpaired electron with the two equivalent  $^{14}\text{N}$  nuclei ( $a_{\text{N}} = 4.2$  Oe), the eight equivalent protons at the 2, 2', 6, 6', 3, 3', 5, 5' positions ( $a_{\text{H}} = 1.4$  Oe), and the two methylene groups (four equivalent protons) of the N- and N'-benzyl substituents ( $a_{\text{H}} = 2.8$  Oe). The splitting of the phenyl ends does not appear under the conditions of the experiment; it introduces a contribution to the width of the individual spectral line. The magnitude of the g-factor of the EPR signal is close to the value for the free electron  $g = 2.0030$ .

The EPR spectra of the remaining compounds were obtained in the form of unresolved singlet lines under analogous conditions. The disappearance of the blue (green) color of the cation-radicals is observed on opening the degassed ampuls in air; the intensity of the signal thereby abruptly decreases to zero in 1-2 min.

The results of the electrolysis at a controlled potential for the first stage of reduction in an inert atmosphere are close to the data of the commutated polarography and EPR spectroscopy; the main product of the electrolysis is the corresponding cation-radical (Table 3).

The number of electrons calculated by the Faraday formula is close to that determined from the classical and commutated polarograms. The primary reduction product — the cation-radical — is present in significant concentrations in the majority of cases on the classical polarograms taken after the electrolysis (Fig. 1, IV); the anodic wave of its oxidation to the initial dication is observable. At potentials which are more negative than the  $E_{1/2}$  of the first and second stages of the reduction of the viologens (I)-(VIII), polarographic waves pertaining to the products of the conversion of the cation-radicals to the corresponding bipyridinium salt are observed. The formation of by-products (with the possible participation of traces of oxygen in the argon) proceeds from the relatively slow reaction following the transfer of the electron during the electrolysis (30 min).

The high degree of the reversibility of the oxidation-reduction processes, the relative stability of the cation-radicals of the viologens, and their bright color permit the use of electrolytes containing the viologens (I)-(VIII) in spectroelectrochemical cells. The record of the composition is held up to  $10^6$  cycles; erasure occurs at the working voltage of 0.8 V and the current-density of  $0.5 \text{ mA/cm}^2$  (ferrocene was employed as an anodic component).

TABLE 3. Results of the Electrolysis at a Controlled Potential of the First Wave of the Reduction of the Bipyridinium Salts ( $E_{1/2}$  is the half-wave potential, V;  $i$  is the limiting current,  $\mu\text{A}$ ;  $n$  are the results of the calculation of the number of electrons according to the formula of Faraday)

Compound	$n$	Characteristics of the polarograms taken after electrolysis					
		$-E_{1/2}$	$i$	$-E_{1/2}$	$i$	$-E_{1/2}$	$i$
I	1.02	0,26	0,40	0,57	0,42	0,83	0,80
II	1,14	0,14	1,40	0,33	1,42	0,78	0,42
IV	1,01	0,16	1,60	0,52	1,40	0,83	1,2
V	0,90	0,17	1,00	—	—	2,10	2,2
VI	0,82	0,26	1,40	0,48	1,30	1,84	1,8
VII	0,82	0,23	1,40	0,53	1,20	1,00	2,0

#### EXPERIMENTAL

The viologens (I)-(VIII) were synthesized according to the methods of [7, 8]. The 0.1 M solution of tetraethylammonium perchlorate in DMFA was utilized as the base electrolyte.

Electrolysis at a controlled potential was performed in a Lingane electrolyzer of total volume 4 ml on platinum wire-gauze electrodes using a P5827 M potentiostat and stirring with a magnetic stirrer in an atmosphere of argon. The time of the electrolysis was 30 min. The concentration of the viologen was  $2 \cdot 10^{-3}$  M. The amount of the electricity was determined by weighing the chart paper under the current-time curve. The classical and cyclic polarograms were plotted under the conditions described in [9].

The EPR spectra were taken in the vacuum of  $10^{-3}$  mm Hg at room temperature using a modified RE-1301 spectrometer (the K-54 klystron with  $\lambda$  3.2 cm; the resolution was 0.1 Oe).

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