4. G. V. Grishina, I. F. Leshcheva, N. M. Sergeev, V. M. Potapov, and A. I. Vovk, Khim. Gerotsikl. Soedin., No. 6, 780 (1982).
5. E. L. Eliel and F. W. Vierhapper, J. Org. Chem., 41, 199 (1977).
6. E. L. Eliel and F. W. Vierhapper, J. Org. Chem., 42, 51 (1977).
7. H. Booth and D. V. Griffith, J. Chem. Soc., Perkin Trans. II, No. 6, 842 (1973).
8. É. A. Mistryukov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 5, 929 (1963).
9. C. A. Grob and H. J. Lutz, Helv. Chim. Acta, 48, 791 (1965).
10. J. H. Grover and J. B. Stothers, Can. J. Chem., 52, 870 (1974).
11. D. Dalling and D. M. Grant, J. Am. Chem. Soc., 95, 3718 (1973).
12. J. W. Blunt, J. M. Coxon, N. Lindley, and G. C. Lone, Aust. J. Chem., 29, 967 (1976).
13. H. Booth, Prog. NMR Spectrosc., 5, 149 (1969).
14. T. Pehk, H. Kooskora, and E. Lippmaa, Org. Magn. Reson., 8, 5 (1976).

INTERMEDIATES IN THE ELECTROLYTIC REDUCTION OF 2-PYRIDYL-1,3-INDANDIONES IN APROTIC MEDIA

Yu. A. Benders, Ya. P. Stradyn', L. M. Baider,
L. Kh. Baumane, and R. A. Gavar

UDC 543.422.27'253:541.138.3:
547.828'665

The character of the products of one-electron reduction of 2-pyridinia-1,3-indandiones (of the phthalone and ylid types) in aprotic media was studied by means of EPR spectroscopy. Free radicals with semidione structures are formed; their hfs constants are presented. Radicals with pyridinium structures are formed only under the condition of the presence of a strong electron acceptor (a cyano group) in the pyridinium ring of the molecule. The formation of unstable intermediates with dimeric structures is postulated as a result of studies by means of cyclical voltammetry.

The one-electron electrochemical reduction of 2-pyridyl-substituted 1,3-indandiones of both the phthalone and ylid types of dimethylformamide (DMF) leads to primary free radicals, for which EPR spectra can be recorded [1-3]. In the present research we attempted to establish the structures of the radicals obtained in the electrochemical reduction of isomeric N-methylpyrophthalones (I), α-N-methylquinophthalone (II), 2-pyridinia-substituted 1,3-indandione onium betaines (ylids III), and 2-methyl-2-pyridyl-1,3-indandione methiodides (IV) to compare the radicals obtained with the products of one-electron reduction of 2-phenyl-1,3-indandiones (V, VI), and to evaluate the stabilities of these radicals and the possibility of their subsequent destruction by dimerization.

The free anion radicals obtained in the electrolytic reduction of 2-pyridyl-1,3-indandiones were found to be extremely similar to the radicals obtained in the electrolytic reduction of 2-phenyl-1,3-indandiones and, at the same time, markedly different from the radicals formed in the electrolytic reduction of pyridinium salts. However, the presence of a pyridinium ring is manifested both in the destruction of the radicals — dimerization takes place in the pyridinium ring — and (for individual representatives of the investigated compounds) in the possibility of delocalization of the unpaired electron on the pyridinium substituent. These peculiarities of the intermediates in the electrolytic reduction of 2-pyridyl-substituted 1,3-indandiones are discussed in the present paper.

Primary Radical Particles

Primary free radicals, viz., products of one-electron reduction of the starting compounds in concentrations sufficient for recording by EPR spectroscopy, were obtained in the electrochemical-generation cell in anhydrous DMF. The primary radicals were obtained at potentials corresponding to the $E_{1/2}$ values of the first polarographic wave of Ia, IIIc, and IVa, b [2,

---

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 237-245, February, 1983. Original article submitted April 22, 1982.

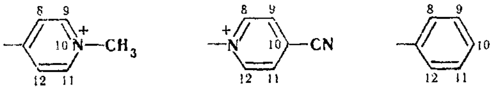
0009-3122/83/1902-0193\$07.50

TABLE 1. Parameters of the hfs and EPR Spectra of the Primary Radical Particles in DMF

Compound	Spectral length, Oe	Character of the splitting	hfs constants, Oe				
			$a_{5,6}^H$	$a_{CH_3}^H$	a^{H*}	a_N	a_{CN}^N
Ic	8,3	$3_H 3_N 4_H 5_H$	2,7	0,6	0,2 ($a_{4,7,9,11}^H$)	0,6	
Ia	5,3	3_H	2,6			†	
II	7,7	$3_H 3_N 4_H 2_H$	2,5	0,3		0,6	
IIIa	4,6	3_H	2,3			†	
IIIb	5,7	$3_H 2_H 3_N$	2,3		0,4	0,4	
IIIc	25,1	$3_N 3_H 3_N 3_H$			3,5 ($a_{8,12}^H$) 0,7 ($a_{9,11}^H$)	6,1	2,0
IVa	5,4	3_H	2,7				
IVb	5,2	3_H	2,6				
V	5,4		2,7				
VI	5,8	$3_H 4_H$	2,4		0,3 ($a_{8,10,12}^H$)		

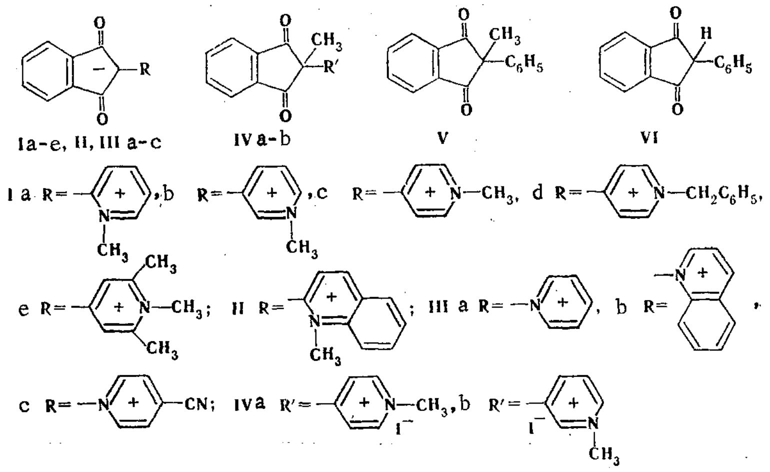
---

*Numbering of the positions for substituent R:



†The EPR spectrum is poorly resolved.

3] and at the potentials of the plateau of the limiting current of the first wave for Ic, II, and IIIa, b. All of the recorded EPR spectra (except for the EPR spectrum of the radical obtained from IIIC) at the resolution and sensitivity of the spectrometer that we used have an hfs that is due primarily to triplet splitting and, in individual cases, also to additional splitting. The principal triplet splitting has a component intensity ratio of 1:2:1 and hfs constants ranging from 2.3 to 2.7 Oe (Table 1).



The previously investigated radicals formed in the electrolytic reduction of 2-phenyl- and 2-methyl-2-phenyl-1,3-indandiones (V, VI) also have the same principal hfs of the EPR spectra [4-6]. The similarity between the hfs of the primary radicals of V and VI and the hfs of the primary radicals of I-IV constitutes evidence that radical particles with semidione structures are generated in both cases, i.e., the unpaired electron is localized primarily on the phthaloyl grouping rather than in the pyridinium part. As in the case of the primary radicals of V and VI, the principal triplet splitting for semidiones I-IV is due to the protons in the 5 and 6 positions of the 1,3-indandionyl fragment.

The $a_{5,6}^H$ values for the semidiones of 2-pyridyl-1,3-indandione depend very little on the heteroaromatic substituent. In addition, the $a_{5,6}^H$ values are close both for the radicals obtained in the electrolytic reduction of the fixed diketo system (IV, V) and the radicals obtained from the compounds with dipolar structures (I, II). The slight dependence of $a_{5,6}^H$ on the character of the substituents in the 2 position is also characteristic for the various anion radicals obtained from derivatives of 2-phenyl-1,3-indandione [4-6] and phthalimide [4].

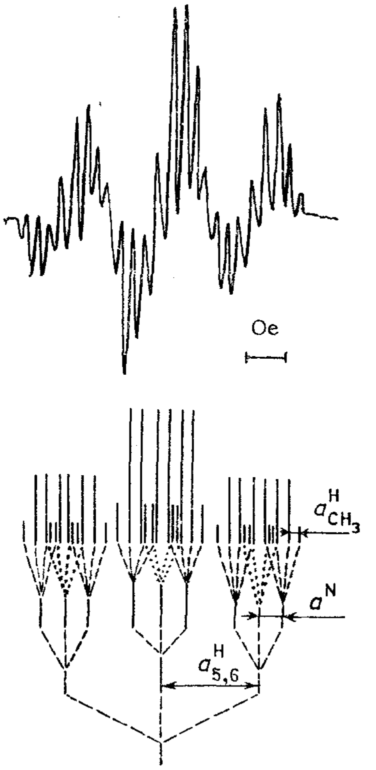


Fig. 1

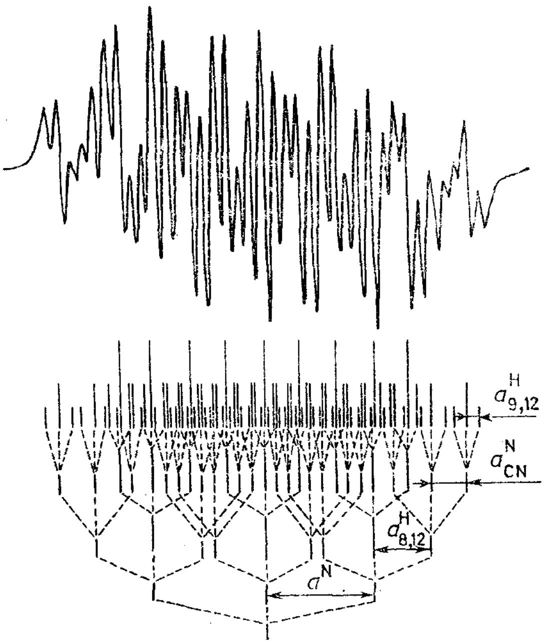


Fig. 2

Fig. 1. EPR spectrum of α-N-methylquinophthalone anion radicals in DMF and its linear reconstruction.

Fig. 2. EPR spectrum of the anion radicals of onium betaine IIIc in DMF and its linear reconstruction.

The $a_{5,6}^H$ values (2.3 Oe) for the anion radicals of the compounds of the ylid type (III) are somewhat lower than for the anion radicals with phthalone structures (from 2.5 to 2.7 Oe) as a consequence of the direct proximity of the positively charged nitrogen atom and the dicarbonyl system.

Depending on the structure of the free radicals, additional splitting may also be observed in addition to the principal splitting by the protons in the 5 and 6 positions. In the case of the primary radicals that are formed from compounds with a fixed dicarbonyl grouping (IV, V) additional splitting is absent: The unpaired electron is localized entirely in the 1,3-indandionyl fragment, which is not conjugated with the pyridinium (phenyl) residue.

However, if the heterocyclic substituent is conjugated with the 1,3-indandione system (I-III), an additional **hfs** due to the nuclei of the heteroaromatic substituent appears distinctly in the EPR spectra of the primary radicals of Ic, II, and IIIb (Fig. 1). The accurate identification of the additional hfs for other compounds of this type is difficult because of inadequate resolution of the EPR spectra. Consequently, the unpaired electron is delocalized over the entire conjugated system in the radicals obtained from the conjugated bases with dipolar structures, viz., phthalones (I, II) and ylids (III). However, judging from the $a_{5,6}^H$ values, the primary localization of the unpaired electron in the 5 and 6 positions that is characteristic for 2-phenyl-1,3-indandione semidiones is also retained in this case.

However, a significant increase in the electrophilicity in the 2 position of the indandione can substantially change the character of the distribution of the unpaired electron. For example, if a strong electron acceptor such as a cyano group is introduced in the 2-pyridinium substituent, the unpaired electron in the corresponding radical is localized exclusively on the pyridinium part (IIIc, Fig. 2). The splitting constants of this anion radical correspond qualitatively to those for 4-cyanopyridine anion radicals [7] and 4-cyano-1-hydropyridinium radicals [8].

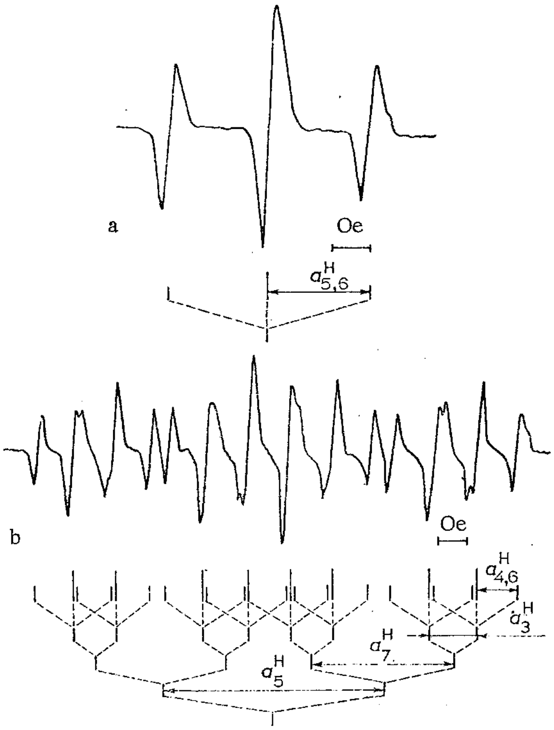


Fig. 3. EPR spectra of the free radicals of the 1-methyl-4-(2-methyl-1,3-dioxo-2-indanyl)pyridinium ion in DMF obtained by electrochemical generation at potentials of −0.1 to −2.0 V (a) and ⩾ −2.1 V (b).

In connection with the possibility of solvation of the radicals by DMF molecules the electrochemical generation of the radical particles was also realized in an aprotic solvent with a lower solvating capacity, viz., acetonitrile [9]. However, as has been demonstrated for the anion radicals of II, IIIa, and IVa, b, the parameters of hfs of the EPR spectra in the two solvents were virtually identical. The change in the solvation of the free radicals in these two solvents is evidently insufficient to attain substantial redistribution of the unpaired electron. The course of the electrolytic reduction of the indicated compounds on a dropping mercury electrode is also identical in both solvents [3].

Stabilities of the Primary Radicals

From the kinetics of attenuation of the EPR signals after removal of the generation voltage we evaluated the stabilities of the primary radical particles of 2-pyridyl-substituted 1,3-indandiones obtained from a compound with a fixed diketo form (IVa), a compound with a dipolar structure (Ic), and 2-phenyl- and 2-methyl-2-phenyl-1,3-indandione (V, VI). It was found that the free radicals of Ic, IVa, and V in DMF decompose via a second-order chemical reaction. However, in the case of 2-phenyl-1,3-indandione radicals the overall destruction of the radical particles is a fractional-order process.

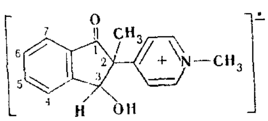
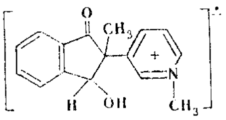
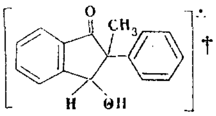
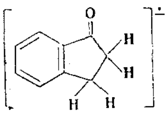
The estimated values of the rate constants of the bimolecular destruction of the radicals are as follows: $1 \cdot 10^3$ liters-mole^{-1}-sec^{-1} for Ic, $2 \cdot 10^2$ liters-mole^{-1}-sec^{-1} for IVa, and $5 \cdot 10$ mole-liter^{-1}-sec^{-1} for V. At a free radical concentration of $1 \cdot 10^{-5}$ mole-liter^{-1} the half lives ($\tau_{1/2}$) of these radicals are, respectively, 100, 500, and 2000 sec. It is apparent that the anion radicals of the compounds with a fixed diketo structure (IVa) are more stable than the radicals obtained from the dipolar compounds (Ic).

The stabilities of the radicals that we investigated evidently considerably exceed the stabilities of the free radicals of pyridinium salts [the rate constants for the dimerization of the radicals of pyridinium salts (N-substituted nicotinamides) determined by cyclical voltammetry in aprotic media range from 10^5 to 10^6 liters-mole^{-1}-sec^{-1} [10]; see the data presented above on the rates of dimerization of the radicals obtained in the present research]. The increase in the stabilities of the primary radicals of 2-pyridyl-substituted 1,3-indandiones is evidently explained by localization of the unpaired electron in the 1,3-indandionyl fragment rather than in the pyridinium fragment.

Radicals with Indandione Structures

Whereas in the case of I-III the radicals indicated above are the only ones that can be recorded, in the case of compounds with fixed structures of the diketo form (IV) radicals with dif-

TABLE 2. Parameters of the EPR Spectra of the Free Radicals with Indanone Structures in Aprotic Media

Radical particles	Solvent	Spectral length, Oe	Character of the splitting	hfs constants, Oe					
				a_2H	a_3H	a_4H	a_5H	a_6H	a_7H
	DMF	21,3	2H2H2H3H	—	4,0	1,0	9,0	1,0	6,1
	Acetonitrile	21,1	2H3H3H	—	3,9	1,9	9,0	1,9	3,9
	DMF	15,2	2H2H3H	—	*	1,7	7,3	1,7	5,6
	Acetonitrile	18,4	2H2H2H3H	—	1,9	1,6	7,4	1,6	5,7
 †	DMF	13,8	2H2H2H3H	—	1,3	1,1	6,4	1,1	4;0
 [11]	DMSO		2H2H2H2H3H3H	13,4	1,6	0,2	6,9	1,5	5,7

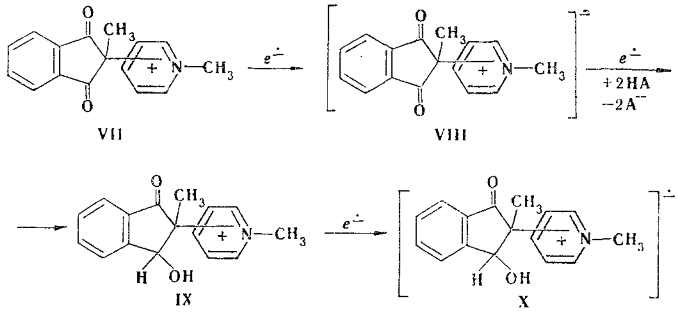
---

*The EPR spectrum is poorly resolved.

†The parameters presented in this table were refined as compared with the data presented in [6].

ferent structures were also recorded by EPR spectroscopy at the potentials of the transfer of a third electron (from −2.1 to −2.4 V). Interaction of the unpaired electron with five protons shows up in the hfs of such radicals (Fig. 3). The formation of two types of radicals was also previously observed for 2-methyl-2-phenyl-1,3-indandione (V) [6].

The radicals detected at −2.1 to −2.4 V are evidently 3-hydroxy-1-indanone anion radicals (X), which are formed as a result of two-electron reduction of one of the carbonyl groups of the 1,3-indandionyl system and subsequent one-electron reduction of the resulting 3-hydroxy-1-indanone (IX) via the scheme



This also confirms the previously proposed (on the basis of polarographic data) mechanism of the electrolytic reduction of these compounds, which involves only the diketo system [3].

The hfs constants of the radicals of the indanone structure are presented in Table 2; the assignment of four of the constants to the protons in the 4–7 positions of the 1-indanone ring was made in analogy with the hfs on the corresponding radical of V. The fifth constant can be assigned to the proton in the 3 position of the indanone ring, which interacts via a hyperconjugation mechanism. This assignment of the hfs constants is in qualitative agreement with the hfs of the previously studied anion radicals of 1-indanone, which have a similar structure [11].

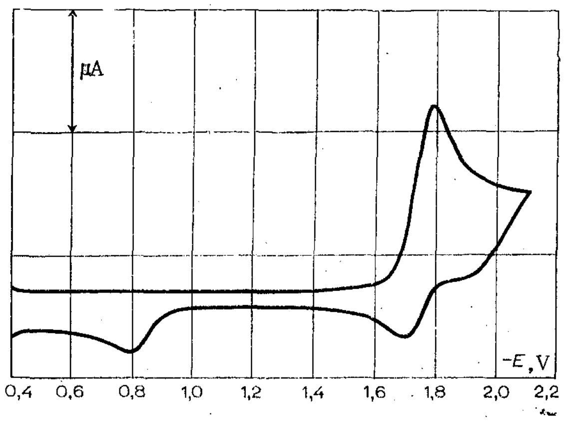


Fig. 4. Cyclical voltammetric curve for γ-N-methylpyrophthanole in DMF at a potential scan rate of 0.5 V/sec.

Replacement of DMF by acetonitrile does not fundamentally change the character of the hfs of these radicals either, although it does lead to a certain change in the hfs constants (Table 2).

The hfs constants due to the protons in the 3-7 positions in the case of the free radicals with indanone structures are considerably more sensitive to a change in the character of the substituents in the 2 position as compared with the radicals with indandione structures. This is possibly due to the fact that in the radicals with indanone structures the single carbonyl group is not in a position to have such a pronounced electron-acceptor effect as the dicarbonyl system in radicals of the semidione type.

Intermediate Particles with Dimeric Structures

It has already been noted that a new polarographic wave with $E_{1/2}$ values ranging from −0.75 to −1.19 V appears in the course of the preparative electrolysis of N-methylpyrophthalones at the potential of the limiting current of the first wave (from −1.64 to −1.79 V) [1]. The new wave becomes larger during the electrolysis and gradually vanishes after electrolysis is discontinued. In the present research we found that this wave does not correspond to a cathode process, as previously assumed, but rather to an anode process (the wave is found below the zero line of the current). This made it possible to assume that secondary intermediates that are capable of electrochemical oxidation are formed as a result of destruction of the primary free radicals.

To ascertain the electrochemical characteristics of these secondary intermediate particles we used polarography and cyclical voltammetry. The presence of secondary reaction products also shows up on the cyclical voltammetric curves of 2-pyridyl-substituted 1,3-indandiones I-III in the form of an additional electrolytic oxidation peak, the E_a values of which range from −0.60 to −0.96 V (Fig. 4 and Table 3). It is apparent that the E_a values of these peaks are more positive than those of the peaks of the electrolytic oxidation of the primary anion radical and that they correspond approximately to the $E_{1/2}$ values of the anode wave that shows up in the case of preparative electrolysis. It should be noted that the peaks of the electrolytic oxidation of such intermediate particles are not recorded during the electrolytic reduction of 2-phenyl-1,3-indandiones in an aprotic medium. We were also unable to detect intermediate particles of this sort in the case of IV, since electrolytic oxidation of the iodide ions occurs over the hypothetical range of the potentials of electrolytic oxidation of these particles.

The formation of the secondary intermediate particles upsets the reversibility of the one-electron reduction of the starting compounds. This is expressed in a decrease in the i_a/i_c values (where i_a and i_c are the currents of, respectively, the peaks of the electrolytic oxidation and reduction of the anion radicals) as the i'_a/i_c values (where i'_a is the current of the peak of the electrolytic oxidation of the intermediate particles, Table 3) increase. The highest i'_a/i_c values, which constitute evidence for the relatively large amount of oxidizable secondary intermediate particles, are characteristic for the cyclical voltammetric curves of Ib, II, and IIIa, for which $i_a/i_c = 0$.

The form of the first polarographic wave of the electrolytic reduction of 2-pyridyl-1,3-indandiones I-III is described by the Koutecky–Hanus equation [12], and the products of reversible one-electron reduction, viz., anion radicals of 2-pyridyl-substituted 1,3-indandiones I-III, consequently undergo a rapid bimolecular reaction.

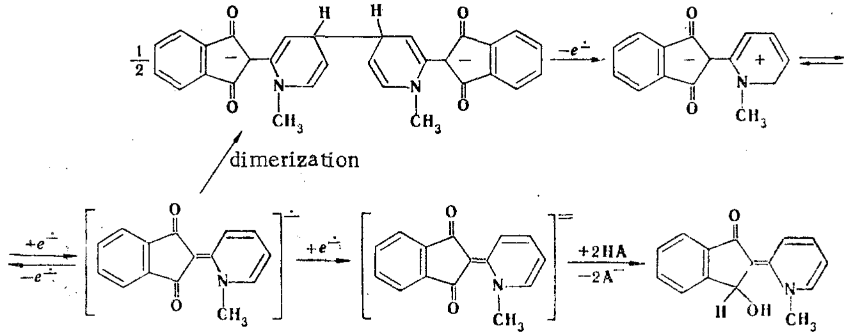
TABLE 3. Potentials of the Cathode (E_c) and Anode (E_a, E'_a) Peaks and Heights of the Cathode (i_c) and Anode (I_a, i'_a) Peaks on the Cyclical Voltammetric Curves in DMF (at the potential scan rate of 0.5 V-sec^{-1}).

Compound	Parameters of the cyclical voltammetric curves				
	$-E_c$, V	$-E_a$, V	$-E'_a$, V	i_a/i_c	i'_a/i_c
Ic	1,78	1,70	0,78	0,33	0,16
Id	1,74	1,66	0,71	0,22	0,22
Ia	1,68	1,58	0,65	0,14	0,25
Ib	1,66	—	0,96	0	0,43
II	1,33	—	0,60	0	0,54
IIIa	1,49	—	0,64	0	0,58

A bimolecular reaction viz., dimerization of the primary radicals, has already been previously observed in the electrolytic reduction of pyridinium salts and 1-methylnicotinamide [10, 13]. The products of dimerization of various pyridinium derivatives that have dihydropyridine structures give, just as in the case of I-III, anode peaks on the cyclical voltammetric curves and anode polarographic waves during preparative electrolysis.

The rate constants for the dimerization of the primary radicals can be calculated by the Nicholson method [14] in our case only for Ic, d, which have a pronounced anode peak of oxidation of the anion radicals. The constants determined by this method were $5 \cdot 10^3$ (Ic) and $7 \cdot 10^3$ moles-liter^{-1}-sec^{-1} (Id), i.e., they are close to the constants for the decomposition of the primary radical of Ic obtained for EPR spectroscopy.

A necessary condition for the dimerization of the primary radicals and the formation of intermediates with dimeric structures for both the pyridinium derivatives and for I-III is the presence of an unsubstituted α position relative to the quaternary nitrogen atom of the pyridinium ring. In the case of dimethyl-substituted pyrophthalone Ie (in which both α positions are substituted) the formation of electrolytic oxidation peaks is not observed on the cyclical voltammetric curves; this constitutes evidence in favor of the formation of dimers involving the pyridinium ring. It may therefore be assumed that the detectable dimers of the investigated compounds have a structure that is similar to the structure of the products of dimerization of the pyridinium derivatives. In the case of Ia the structure of the dimer is depicted in the electrolytic reduction scheme:



In the case of the free radicals of conjugates I-III the unpaired electron is also delocalized, although to a very slight extent, on the pyridinium part, and this is responsible for the possibility of dimerization involving the pyridinium ring.

This unexpected (at first glance) sequence of the electrochemical reduction of 2-pyridyl-1,3-indandiones, in which the phthaloyl grouping is reduced more readily on a dropping mercury electrode than the positively charged pyridinium fragment can be explained by the high electrophilicity of 1,3-indandione and, in the case of dipolar compounds, also by the possibility of the existence of conjugated structures of the 1,4-dihydropyridinium type [15].

EXPERIMENTAL

Compounds I-VI were synthesized by the methods in [16-19].

The electrochemical reduction of the investigated compounds was carried out in anhydrous dimethylformamide (DMF) and acetonitrile with tetrabutylammonium perchlorate (0.1 mole-liter^{-1}) as the inert electrolyte. The depolarizer concentration was $5 \cdot 10^{-4}$ mole-liter^{-1} during recording of the cyclic voltammetric curves and 10^{-3} mole-liter^{-1} during electrochemical generation of the free radicals. The classical polarograms were recorded by means of the PAR-170 electrochemical system with the aid of a three-electrode cell. The cyclical voltammetric curves were obtained with the same apparatus with the aid of a stationary electrode, viz., a suspended mercury drop.

The free-radical particles of the investigated compounds were obtained by electrochemical generation via a three-electrode scheme on the surface of a plane platinum electrode (the reference electrode was a platinum wire) in a microcell placed in the resonator of a Karl Zeiss ER-9 EPR spectrometer (Jena) in DMF and acetonitrile.

The rate constants for destruction of the free-radical particles were determined from the attenuation of the EPR signal after feeding of voltage to the electrochemical generation cell was discontinued. The rate constants for destruction of the radicals were determined graphically in accordance with the second-order reaction equation. The initial concentrations of the radicals were determined by calibration with the aid of the stable 2,2,6,6-tetramethyl-4-oxopiperidine oxide radical as the standard.

LITERATURE CITED

1. Ya. P. Stradyn', V. P. Kadysh, L. M. Baider, É. S. Lavrinovich, and Yu. É. Fridmanis, Khim. Geterotsikl. Soedin., No. 8, 1097 (1977).
2. V. P. Kadysh, Ya. P. Stradyn', Yu. A. Benders, and O. Ya. Neiland, Khim. Geterotsikl. Soedin., No. 3, 369 (1980).
3. Yu. A. Benders, Ya. P. Stradyn', and Ya. Ya. Katsen, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 1, 107 (1981).
4. S. F. Nelson, J. Am. Chem. Soc., 89, 5256 (1967).
5. R. E. Syuda and W. S. Koski, J. Am. Chem. Soc., 89, 475 (1967).
6. R. A. Savar, Yu. A. Bender, L. Kh. Baumane, and Ya. P. Stradyn', Zh. Obshch. Khim., 43, 1584 (1973).
7. M. Itoh and S. Nagakura, Tetrahedron Lett., No. 8, 417 (1965).
8. J. K. Dohnman and R. Becker, J. Magn. Reson., 27, 371 (1977).
9. V. Gutman, Electrochim. Acta, 21, 661 (1976).
10. K. S. V. Santhanam and P. J. Elving, J. Am. Chem. Soc., 95, 5482 (1973).
11. S. F. Nelson, J. Org. Chem., 38, 2693 (1973).
12. J. Koutecky and V. Hanus, Collect. Czech. Chem. Commun., 20, 124 (1955).
13. I. Carelli, M. E. Cardinali, and F. M. Moracci, J. Electroanal. Chem., 107, 391 (1980).
14. M. L. Olmstead, R. G. Hamilton, and R. S. Nicholson, Anal. Chem., 41, 260 (1969).
15. I. Amiel, I. Ploquin, L. Sparfel, G. Le Baut, and R. Floch, Bull. Soc. Chim. Fr., Nos. 9-10, 2154 (1974).
16. É. S. Lavrinovich and Yu. É. Fridmanis, USSR Inventor's Certificate No. 556140; Byull. Izobret., No. 16, 66 (1977).
17. R. Kuhn and F. Bar, Ann. Chem., 516, 155 (1935).
18. I. K. Raiskuma, G. G. Pukitis, and O. Ya. Neiland, Khim. Geterotsikl. Soedin., No. 7, 889 (1978).
19. Yu. É. Fridmanis and L. P. Osis, in: Second Republican Conference of Young Scientists and Chemists [in Russian], Vol. 1, Tallin (1977), p. 7.