18. H. Fischer and H. Ort, The Chemistry of Pyrrole [Russian translation], Leningrad (1937), p. 143.
19. A. Treibs and G. Fritz, Ann., 611, 162 (1958).
20. G. M. Badger, R. L. Harris, and R. A. Jones, Austr. J. Chem., 17, 1022 (1964).
21. S. D. Mikhno, T. M. Filippova, N. S. Kulachkina, I. G. Suchkova, and V. M. Berezovskii, Khim. Geterotsikl. Soedin., No. 3, 331 (1976).
22. V. I. Bogomolov and Kh. M. Minachev, in: Molecular Chromatography [in Russian], Nauka (1964), p. 10.
23. Organic Syntheses [Russian translation], Collective Vol. 3, Inostr. Lit., Moscow (1952), p. 512.

POLAROGRAPHIC REDUCTION OF 2-(4-PYRIDYL)INDANE-1,3-DIONES IN DIMETHYLFORMAMIDE

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L. M. Baider, É. S. Lavrinovich,
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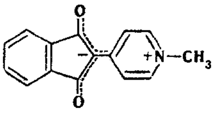
UDC 543.253 : 547.828 : 543.422.27

The trend of the electrical reduction of isomeric 2-(4-pyridyl)indane-1,3-diones in dimethylformamide (DMF) was studied by classical and ac polarography, millicoulometry, ESR spectroscopy, and cyclical voltamperometry with a steady-state mercury electrode. The first reversible one-electron step leads to the formation of relatively stable anion radicals, which can be recorded by means of ESR spectroscopy. The corresponding dimers are detected in the course of prolonged electrolysis at a constant potential (at the level of the limiting current of the first wave). The second nonreversible step in the electrical reduction involves the indane-1,3-dionyl grouping and the pyridinium ring. Owing to their dipolar structure, the investigated compounds are reduced with considerably greater difficulty (by 400-550 mV) than the unsubstituted N-methylpyridinium salt.

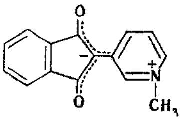
The set of chemical transformations in the reduction of 2-(4-pyridyl)indane-1,3-diones (which are usually called pyrophthalones) has not yet been ascertained [1], despite the fact that the reduction products could have diversified biological activity.

Pyrophthalones are also of interest in the respect that their molecules contain two potentially electrically active fragments – the pyridinium ring and the indane-1,3-dionyl grouping,* which can undergo reduction either separately or as a unified conjugated system. In view of the above, within the framework of our systematic research on the reduction of substituted pyridinium salts [3, 4], we also studied the mechanism of the electrical reduction of pyrophthalone derivatives in order to find their quantitative characteristics – the reduction potentials for the primary electrical reduction steps.

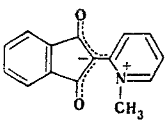
In the present research we obtained the electrochemical characteristics of Ia-d in nonaqueous media (Table 1) by means of classical and ac polarography, millicoulometry, ESR spectroscopy, and cyclical voltamperometry with a steady-state mercury electrode. The quaternized compounds were selected to avoid the formation of catalytic hydrogen waves and the effects of intra- or intermolecular protonation during electrical reduction.



Ia



Ib



Ic

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* This grouping is more accurately called an indane-1,3-dionide grouping, since it may be assumed that pyrophthalones exist in the form of betaine structures [2].

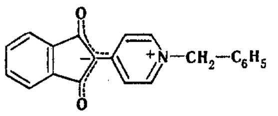
Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Geterotsiklicheskikh Soedinenii, No. 8, pp. 1097-1102, August, 1977. Original article submitted August 23, 1976.

TABLE 1. Half-Wave Potentials ($E_{1/2}$) and Limiting Currents (i_{lim}) for Derivatives of 2-(4-Pyridyl)indane-1,3-diones and Compounds Modeling the Two Electrically Active Systems Included in Their Composition in DMF with a 0.1 N Tetrabutylammonium Perchlorate Base Electrolyte

Compound	Name	Wave I		Wave II		Wave III	
		$-E_{1/2}$, V	i_{lim}, μA	$-E_{1/2}$, V	i_{lim}, μA	$-E_{1/2}$, V	i_{lim}, μA
Ia	1-Methyl-4-[2'-indane-1,3-dionid-2-yl]pyridinium	1,79	1,00	2,24	1,75	2,57	0,75
Ib	1-Methyl-3-[2'-indane-1,3-dionid-2-yl]pyridinium	1,64	1,10	2,36	2,10	—	—
Ic	1-Methyl-2-[2'-indane-1,3-dionid-2-yl]pyridinium	1,68	1,10	2,34	2,40	—	—
Id	1-Benzyl-4-[2'-indane-1,3-dionid-2-yl]pyridinium	1,74	1,10	2,22	1,70	~2,36	Weakly expressed
IIa	2-Phenylindane-1,3-dione	1,23	0,62	2,24	0,97	—	—
IIb	Tetrabutylammonium 2-phenylindane-1,3-dion-2-ide	—	—	2,27	1,15	—	—
III	1-Methylpyridinium iodide	1,22	1,15	—	—	—	—
IV	2,2'-Bis[2-(4-pyridyl)indane-1,3-dionyl]	1,01	0,55	2,20	0,40	2,75	0,40
V	2,2'-Bis[2-(3-pyridyl)indane-1,3-dionyl]	1,09	0,40	2,27	0,45	2,81	0,30

TABLE 2. Calculation of the Number of Electrons by Means of Controllable-Potential Electrolysis for the First (n_1) and Overall (n_Σ) Waves

Compound	n_1	$-E_1$, V	n_Σ	$-E_\Sigma$, V
Ia	1,91	2,0	5,78	2,75
Ib	1,18	1,9	2,71	2,60
Ic	0,93	1,75	2,99	2,60



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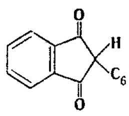
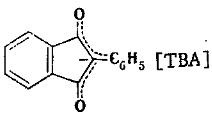
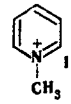


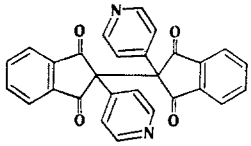
IIa



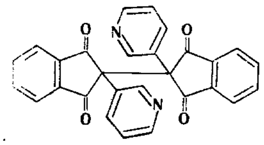
IIb



III



IV



V

Somewhat simpler compounds (IIa,b and III) that model the individual fragments of the Ia-d molecules and the corresponding dimers (IV, V) were also additionally investigated under identical experimental conditions.

It is apparent from a comparison of the i_{lim} and $E_{1/2}$ values (Table 1) that Ib-d give two and Ia gives three well-expressed waves on their classical polarograms, and the height of the second wave exceeds the height of the first wave by, on the average, a factor of two (Fig. 1, curve a). The direct proportionality of the i_{lim} values of both waves to the square root of the height of the mercury column constitutes evidence for the diffusion character of both waves.

The results of the millicoulometric measurements are presented in Table 2. The higher number of electrons (n) expended in the reduction of Ia as compared with Ib and Ic is due to the fact that the electrolysis at a controllable potential for the calculation of the overall n value was carried out at the potential of the plateau of the limiting current of the third wave, whereas electrolysis was carried out at the level of the second wave for Ib and Ic, i.e., for Ia, in which conjugation is maximally expressed, one of the steps of subsequent reduction of the radical to dihydropyridine and indanonol, which we do not note in the case of Ib and Ic, is recorded.

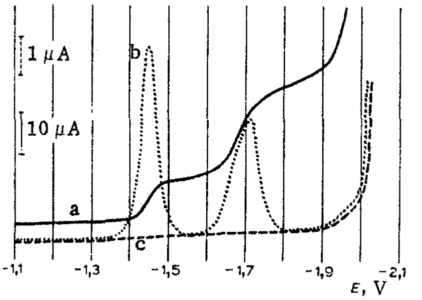


Fig. 1

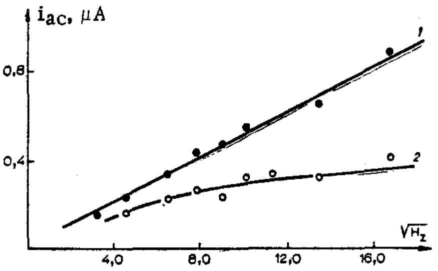


Fig. 2

Fig. 1. Polarographic curves of 1-methyl-4-[2'-indane-1,3-dionid-2-yl]-pyridinium in DMF with a 0.1 N tetrabutylammonium perchlorate base electrolyte (depolarizer concentration $5 \cdot 10^{-4}$ mole/liter): a) dc; b) ac; c) base electrolyte.

Fig. 2. Dependence of the magnitude of the alternating current on the frequency for the first (1) and second (2) waves of 1-methyl-4-[2'-indane-1,3-dionid-2-yl]pyridinium in DMF with a 0.1 N tetrabutylammonium perchlorate base electrolyte (depolarizer concentration $5 \cdot 10^{-4}$ mole/liter).

Reversibility of the Electrochemical Reduction and Adsorption of Compounds on the Electrode

Two peaks corresponding to the waves on the classical polarograms are observed on the Breier ac polarograms of Ia-d. The peak of the first wave is symmetrical relative to the potential of the peak (E_n), and the E_n value coincides with $E_{1/2}$, and the width of the half-peak ($E_n/_2$) is 88 mV; this is in conformity with a strictly reversible process (Fig. 1, curve c).

The E_n value of the first wave is shifted slightly (by ~15 mV) from the frequency of the ac voltage to more positive potentials, and its height changes linearly with the frequency (Fig. 2); this also indicates reversibility of the first wave. The results of ac polarography relative to the second wave (Fig. 2) provide unambiguous evidence for irreversibility of this wave.

A peak corresponding to the third wave shows up for Ia when $E_n = -2.58$ V; however, the height of this peak is almost one-tenth of the height of the first peak, and $E_n/_2$ is 115 mV; this constitutes evidence for irreversibility of this wave.

Neither an increase nor a decrease in the principal current is noticeable in the presence of the investigated compounds, i.e., the levels of the ac polarograms in the range of potentials prior to the onset of reduction and after it coincide with the level of the current of the base electrolyte over the same range of potentials (Fig. 1, curve c). According to Breier [5], this constitutes evidence for the absence of absorption on the electrode of both the starting depolarizer and its reduction products. The dielectric constant of DMF is, of course, lower than that of water, and the regularity may therefore be expressed to a lesser extent in DMF solutions. The direct proportionality of the heights of both concentration waves of the substances over a broad range of concentrations also attests to the absence of appreciable adsorption effects.

Two cathode peaks (A and B), the E_n values of which correspond to the $E_{1/2}$ values of the waves on the classical polarograms, are observed on the cyclical polarograms (Fig. 3) of I obtained with a suspended mercury drop at potentials from −0.3 to −2.7 V at a polarization rate of 1 V/sec.

In addition to the two above-mentioned peaks on the cyclical voltamperograms at −0.62 V, peak C appears at −0.68 V in the case of cathode polarization. Both peaks increase with time, and whereas peak C shows up in the first cycle, peak D shows up in the subsequent cycles and is a consequence of the development of peak C. Peaks C and D appear only if the electrochemical reaction goes to completion, i.e., polarization occurs in the interval −0.3 to −2.7 V. However, the C and D peaks are not observed when only the first wave of electrochemical reduction is recorded (Fig. 3, curve 1). Peak C evidently corresponds to oxidation of the product of the final electrochemical reaction, and peak D corresponds to the subsequent reduction of the oxidized product.

The addition of proton donors has a substantial effect on the reduction of Ia-d. Thus when phenol is

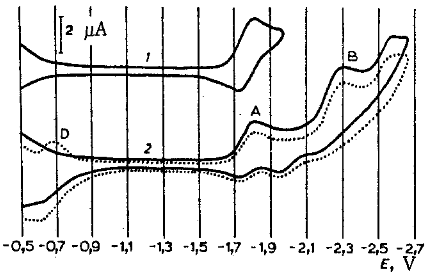


Fig. 3

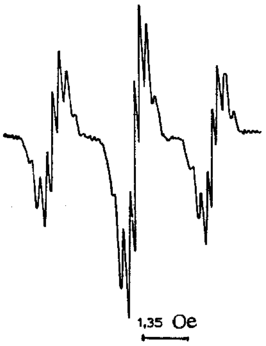


Fig. 4

Fig. 3. Voltamperometric current–potential curves for 1-methyl-2-[2'-indane-1,3-dionid-2-yl]pyridinium recorded with a suspended mercury drop in DMF with a 0.1 N tetrabutylammonium perchlorate base electrolyte at a polarizer interval of $5 \cdot 10^{-4}$ mole/liter and a scanning rate of 1 V/cm. Polarization range: 1) from −0.5 to −2.0 V; 2) from −0.5 to −2.7 V.

Fig. 4. ESR spectra of the anion radical of 1-methyl-4-[2'-indane-1,3-dionid-2-yl]pyridinium recorded in DMF with a 0.1 N tetrabutylammonium perchlorate base electrolyte at a salt concentration of $2 \cdot 10^{-3}$ mole/liter.

added, the height of the first wave remains practically unchanged, whereas the second wave increases sharply. The $E_{1/2}$ values of the first wave change only slightly, whereas those of the second wave are shifted by 60 mV to the positive side in the case of Ic as the phenol concentration in the solution is increased to $5 \cdot 10^{-3}$ mole/liter.

Products of One-Electron Transfer

The ESR spectra recorded under the conditions of electrochemical generation of radicals at the potentials of the plateau of the limiting current of the first wave for Ia-c and of the corresponding pyrophthalones (without a methyl group attached to the pyridinium nitrogen atom) prove the formation of free anion radicals, during the electrical reduction, that are sufficiently stable for recording by ESR spectroscopy. The hyperfine structure (hfs) of the ESR spectra consists of a triplet with an intensity ratio of the individual components of 1 : 2 : 1 and an hfs constant of 2.6 Oe, whence it follows that the unpaired electron is localized primarily in the 5 and 6 positions of the indanedionyl portion, as in 2-phenylindane-1,3-dione semidiones [6]. It was concluded from a comparison of the polarographic data and the hfs of the ESR spectrum that the first step in the electrochemical reduction involves the entire conjugated system as a whole with the formation of a relatively stable free radical.

We were able to observe splitting on the atoms of the pyridinium ring only in the case of the electrical reduction of Ia (Fig. 4) and the corresponding pyrophthalone. The hfs constants are small (~ 0.2 Oe). Unfortunately, analysis of the hfs of the ESR spectra does not make it possible to sufficiently reliably assign this constant to the nitrogen atom or to the protons in the α position of the pyridinium ring. Under the experimental conditions without low-temperature stabilization we also did not observe a substantial difference in the stabilities of the anion radicals obtained during the electrical reduction of Ia-c (as well as of the corresponding anion radicals obtained in the reduction of the unmethylated analogs).

It is important to note that in the case of controllable-potential electrolysis (CPE) of Ia-c an additional wave with a more positive $E_{1/2}$ value (−0.75 V for Ia, −1.19 V for Ib, and −0.79 V for Ic) appears; this wave falls rapidly with time (30 min after CPE, it vanishes completely). The wave reappears upon resumption of CPE (without the addition of a new portion of the compound), i.e., it is a consequence of reduction of the product of a chemical reaction. We assumed that it shows up as a result of cleavage of the C–C bond in the dimers formed as a result of dimerization of the anion radicals after the first step in the electrochemical reduction of the investigated compounds.

The reductive cleavage of the C–C bond in diphenylindane-1,3-diones (at sufficiently positive potentials) was demonstrated in [7]. In our case the $E_{1/2}$ values of the additional waves that appear as CPE is carried out are rather close to the $E_{1/2}$ values of the first wave of model dimeric compounds IV and V (Table 1); this confirms the assumption of the formation of dimers and, consequently, anion radicals as intermediates in the electrical reduction.

As seen from Table 1, the half-wave potentials of the second wave of Ia-d coincide satisfactorily with the half-wave potentials of IIb and the second wave of IIa, which in DMF exists partially in the anionic form [7]. The subsequent reduction of the resulting anion radical evidently involves the indanedione fragment, and in this case the process takes place with prior protonation of the anion radical, as indicated by the pronounced effect of the addition of a proton donor on the character of the second wave, and the electrochemical reduction corresponding to the second wave of the investigated compounds is consequently in agreement with the mechanism of the electrical reduction of the enolate anions of 2-phenylindane-1,3-dione and leads to anions with a dienediol structure [8].

The validity of this conclusion is confirmed by the presence on the cylical polarograms of both the investigated compounds and IIa of anode peak C at ~ -0.6 V, which shows up as a consequence of oxidation of the products with a dienediol structure, which were described for the first time in the case of the electrical reduction of IIa in [9].

Structural Effects

A comparison of the polarographic behavior of Ia-d with the polarographic behavior of N-methylpyridinium cations and anions IIa showed that the effect of the pyridinium fragment of the molecule (the 450-600 mV shift of $E_{1/2}$ to the positive side due to the presence of the positive charge of the quaternary nitrogen atom) is somewhat greater than the effect of the negatively charged indane-1,3-dione fragment, which shifts the $E_{1/2}$ value by 400-550 mV to the negative side as compared with the unsubstituted salt. The predominant role of the charge of the grouping introduced into the molecule is made apparent in both comparisons, i.e., the specific character of the dipolar structure is manifested.

The half-wave potentials of Ia,b do not fit on the general correlation curve of the dependence of the $E_{1/2}$ values of substituted pyridinium salts on the σ substituent constants when the σ constants in [10] are assumed for the indane-1,3-dionyl group. This constitutes evidence that the mechanism of the electrical reduction of the investigated compounds with a dipolar structure differs from the mechanism of the electrical reduction of pyridinium salts.

As a result of the pronounced effect of the negatively charged indanedione fragment on the shift of the $E_{1/2}$ values to the negative side, a change in the position of the pyridinium group and a change in the character of the substituent attached to the nitrogen atom in the pyridine ring do not have a substantial effect on the half-wave potentials.

EXPERIMENTAL

The polarographic investigation of I-V (the synthesis of the compounds will be published separately) was carried out in anhydrous DMF; recrystallized samples were used. Tetrabutylammonium perchlorate, prepared by the method in [11], was used as the inert electrolyte. The depolarizer concentration was $5 \cdot 10^{-4}$ mole/liter in all cases, and the ionic strength was 0.1.

The polarographic studies were carried out with a PAR-170 electrochemical system with a three-electrode scheme manufactured in the workshops of Princeton University. The working electrode was a dropping mercury electrode with forced drop detachment ($t = 0.5$ sec and $m = 0.69$ mg/sec), the anode was platinum wire, and the comparison electrode was an aqueous saturated calomel electrode.

The cyclical volt–ampere curves were obtained with a steady-state electrode – a model 9323 suspended mercury drop with a surface area of 2.87 mm^2.

LITERATURE CITED

1. O. Ya. Neiland and Ya. Ya. Katsen, Khim. Geterotsikl. Soedin., No. 4, 435 (1975).
2. J. Ploquin et al., Europ. J. Med. Chem., Chimica Therapeutica, 9, 526 (1974).
3. V. P. Kadysh, Ya. P. Stradyn', É. S. Lavrinovich, and P. P. Zarin', Khim. Geterotsikl. Soedin., No. 5, 675 (1975).

4. Ya. P. Stradyn', V. P. Kadysh, and S. A. Giller, Khim. Geterotsikl. Soedin., No. 12, 1587 (1973).
5. P. Zuman and I. M. Kolthoff (editors), Progress in Polarography, Vol. 2, New York–London (1962), p. 487.
6. R. A. Gavar, Yu. A. Bender, L. Kh. Baumane, and Ya. P. Stradyn', Zh. Obshch. Khim., 43, 1584 (1973).
7. Ya. Stradyn', I. Tutane, O. Neiland, and G. Vanag, Dokl. Akad. Nauk SSSR, 166, 631 (1966).
8. Ya. P. Stradyn' and V. P. Kadysh, Coll. Czech. Chem. Commun., 36, 698 (1971).
9. I. K. Tutane and Ya. P. Stradyn', Élektrokhimiya, 4, 398 (1968).
10. Ya. P. Stradyn', I. Ya. Kravis, and A. K. Grinvalde, Summaries of Papers Presented at the Fourth All-Union Conference on the Chemistry of Dicarbonyl Compounds [in Russian], Riga (1976), p. 158.
11. H. O. House, E. Feng, and N. P. Peet, J. Org. Chem., 36, 2371 (1971).

HETERORING CONTRACTION IN 1-DIAZOANTHRAPYRIDONE*

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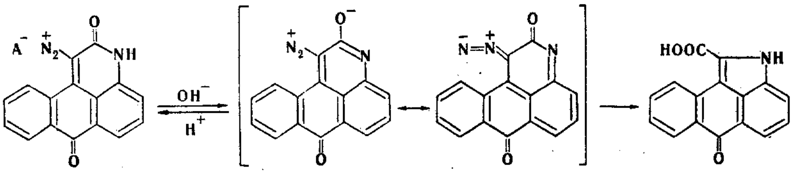
and E. G. Kuznetsova

UDC 547.75:542.952

Anthrapyridone-1-diazonium salts are converted with ring contraction to pyrroloanthrone-1-carboxylic acid and, in the presence of alcohols, to its esters.

Pyrroloanthrone (6H-naphth[1,2,3-cd]indol-6-one) and its derivatives are difficult to obtain, and little study has been devoted to them. We have found a new method for the preparation of this heterocyclic polycondensed system – contraction of the ring in anthrapyridone-1-diazonium salts (1-diazo-7H-dibenz[f,ij]isoquinoline-2,7[3H]-dione) (I) to give pyrroloanthrone-1-carboxylic acid (II). Since, as shown in [2], the starting 1-aminoanthrapyridine and its substituted derivatives are extremely accessible, this method may have preparative value.

Salts I, which we obtained for the first time in the form of the hydrosulfates, tetrafluoroborates, and perchlorates, are stable crystalline substances. They undergo conversion to acid II even when they are dissolved in water, and the reaction is accelerated by the addition of alkalis, heating, and irradiation with daylight or UV light. The reaction proceeds instantaneously in strongly alkaline media, but small amounts of impurities (primarily 1-hydroxyanthrapyridone) are observed in this case. To reduce the amount of impurities and achieve high yields of acid II, it is expedient to carry out the reaction under the influence of weaker alkaline agents (for example, alkali-metal acetates or carbonates) and in mixtures of water and organic solvents. Derivatives of acid II that contain substituents in the anthrone fragment can also be obtained under the same conditions, as shown in the case of the synthesis of 3-methyl-5-bromopyrroloanthrone-1-carboxylic acid (III) (Table 1).



I VII II

The structure of product II was proved by decarboxylation to pyrroloanthrone IV and subsequent arylation with bromobenzene to give N-phenylpyrroloanthrone V, which was identical to the substance synthesized by an independent method by cyclization of N-(1-anthraquinonyl)-N-phenylglycine VI [3].

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[*] See [1] for our preliminary communication.

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1103-1105, August, 1977. Original article submitted November 17, 1975.