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# POLAROGRAPHIC REDUCTION OF NONQUATERNIZED AND QUATERNIZED PYROPHTHALONES IN PROTOGENIC MEDIA

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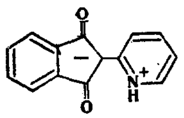
The polarographic reduction potentials were determined by classical polarography, millicoulometry, preparative electrolysis, and cyclical voltammetry, and the course of the electrochemical process for nonquaternized and quaternized pyrophthalones in 20% buffer solutions in aqueous dimethylformamide was studied. In the case of α and γ isomers of pyrophthalones, two-electron irreversible electrical reduction leads to the formation of an indan-1-on-3-yl-1,4-dihydropyridine, which exists in two protolytic forms. The compound was isolated and its structure was proved by means of mass spectrometry. The polarographic reduction of β-pyrophthalones is similar to the electrical reduction of 2-phenylindane-1,3-dione. The tautomeric-protolytic equilibria of quaternized and nonquaternized α-, β-, and γ-pyrophthalones were studied, and it was ascertained that individual tautomeric-protolytic forms participate in the electrochemical process at various pH values.

Various products are formed in the reduction of 2-pyridylindane-1,3-diones (all of the isomers, which we have designated by the general term "pyrophthalones" [1]); depending on the reduction conditions, either the indanedionyl or pyridinium fragment of the molecule, or both, are involved [2].

To characterize the individual possible steps in the reduction, and to determine the corresponding electrode potentials, we chose a polarographic method and undertook a systematic polarographic study of diverse pyrophthalones.

Rather stable anion radicals, the unpaired electron in which is localized primarily in the 5 and 6 positions of the indanedionyl fragment of the molecule, are formed in the polarographic reduction of quaternary isomeric 2-pyridylidane-1,3-diones in aprotic dimethylformamide (DMF) media as a result of transfer of the first electron [3]. The next step in the electrical reduction involves the indanedionyl fragment of the molecule and only at extremely negative potentials, and the pyridinium fragment of the molecule evidently also undergoes reduction.

As a rule, the transition from aprotic to protogenic media gives rise to more profound destruction of the starting molecules during the electrical reduction of organic compounds.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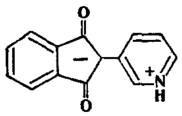
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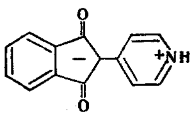
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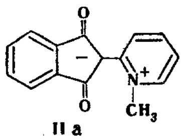
IIa

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Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 218-227, February, 1980. Original article submitted June 18, 1979.

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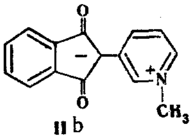

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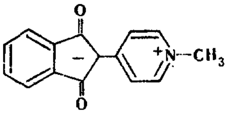

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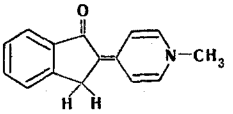
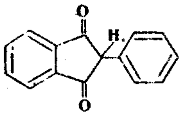
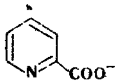


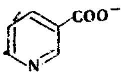
III



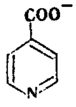
IV



Va



Vb



Vc

In particular, this was demonstrated for 2-arylidane-1,3-diones [4]. In the case of pyrophthalones Ia-c and IIa-c reduction should proceed differently as a function of protonation of the starting dipolar ion and protonation of the intermediates in the reduction (for example, III).

In the present communication we present the results of a polarographic study of isomeric pyrophthalones Ia-c and their quaternary (methyl) derivatives IIa-c in protogenic (aqueous organic) media. To make it possible to compare the pyrophthalones with model compounds, viz., 1-methyl-4-(1-oxo-2-indanylidene)-1,4-dihydropyridine (III), 2-phenylidane-1,3-dione (IV), and derivatives of pyridinecarboxylic acids (V), the latter were studied under similar conditions.

To form a judgment regarding the protolytic forms of pyrophthalones that actually exist in solution, during this study we ascertained the corresponding tautomeric-protolytic equilibria in solutions of pyrophthalones. For solubility reasons, the study of all of the compounds was made in 20% aqueous dimethylformamide (DMF) Britton–Robinson buffer mixtures at various pH values. The numerical $i_{lim}$ and $E_{1/2}$ values of the first reduction waves of I-V are presented in Table 1.

## General Picture of Electrical Reduction in 20% Aqueous DMF Britton–Robinson Buffer Solutions

Nonquaternized and Quaternized Pyrophthalones. Three waves – A, B, and C (Fig. 1) – are observed for the investigated quaternized pyrophthalones, depending on the pH value, while A, B, and D waves are observed for the nonquaternized pyrophthalones I. The polarographic behavior of β-pyrophthalone (Ib) and β-methylpyrophthalone (IIb) differs substantially from the behavior of the α and γ derivatives.

The A wave is observed for the α and γ derivatives of the nonquaternized and quaternized pyrophthalones over the entire investigated pH range from two to 12, while wave B is observed only in acidic media. The dependence of $i_{lim}$ on the height of the mercury column, the temperature, and the depolarizer concentration indicates the diffusion character of the A wave for both pyrophthalone I and for II. In the case of α-pyrophthalones the height of the A wave does not change substantially over the entire investigated pH range, and the number (n) of electrons for the A wave in the case of Ia is 2.20 (pH 2.5) and 2.00 (pH 7.0), as compared with 2.25 and 1.95 in the case of IIa. On the other hand, an appreciable increase in the A wave in acidic media is observed for γ-pyrophthalones; n is 2.64 (pH 2.5) and 1.91 (pH 7.0) in the case of Ic, as compared with 3.00 and 2.30, respectively, in the case of IIc. The dependence of $E_{1/2}$ of the A wave on the pH for α- and γ-pyrophthalones has an S-shaped character (Fig. 1).

On the short-period mercury electrode used in our principal studies the B wave for the α and γ derivatives is considerably lower than the A wave and shows up only at pH 2-5.5. As the pH increases, the B wave becomes smaller and takes on a partially kinetic character. The dependence of $i_{lim}$ of the B wave on the pH changes substantially as a function of dropping time t. As t increases, in addition to an increase in the height of the wave (in the case of IIc even up to the height of the A wave), it is observed over a broader pH range up to pH 7.0; moreover, the dependence of $i_{lim}$ on the pH takes on the form of the dissociation curve with polarographic protolysis constant ($pK_{pol}$) $\approx$ 4.0. In addition to the usual criteria, the increase in exponent x in the equation $i_{lim} = at^x$ indicates the diffusion character of this wave (x increases from 0.22 at pH 2.2 to 0.57 at pH 5.5 as the pH increases).

TABLE 1. Half-Wave Potentials and Limiting Currents of I-V in Britton-Robinson Buffer Solutions (20% DMF) at Various pH Values and a Depolarizer Concentration of $5 \cdot 10^{-4}$ mole/liter

| Compound | pH | $E_{1/2}$, V | | | $i_{lim}$, μA | | |
|---|---|---|---|---|---|---|---|
| | | wave | | | | | |
| | | A | B | C | A | B | C |
| I a | 2,5 | 0,80 | 1,04 | | 1,50 | 0,84 | |
| | 3,5 | 0,85 | 1,08 | | 1,44 | 0,55 | |
| | 4,5 | 0,92 | 1,14 | | 1,36 | 0,40 | |
| | 6,0 | 1,08 | | 1,57 | 1,34 | | 6,7 |
| | 7,5 | 1,20 | | 1,64 | 1,35 | | 2,5 |
| | 8,5 | 1,25 | | 1,67 | 1,34 | | 1,9 |
| | 9,5 | 1,32 | | 1,69 | 1,38 | | 1,8 |
| I b | 2,5 | 0,86 | 1,22 | | 1,48 | 0,33 | |
| | 3,5 | 0,92 | 1,24 | | 1,48 | 0,64 | |
| | 4,5 | 1,00 | 1,32 | | 1,54 | 0,92 | |
| | 6,0 | 1,13 | 1,40 | 1,72 | 1,08 | 1,04 | ~10 |
| | 7,5 | | 1,48 | 1,70 | | 2,00 | ~3 |
| | 8,5 | | 1,52 | | | 1,90 | |
| | 9,5 | | 1,54 | | | 1,67 | |
| I c | 2,5 | 0,76 | 1,03 | | 1,89 | 0,51 | |
| | 3,5 | 0,82 | 1,05 | | 1,60 | 0,54 | |
| | 4,5 | 0,86 | 1,08 | | 1,50 | 0,50 | |
| | 6,0 | 1,00 | | 1,58 | 1,22 | | ~15 |
| | 7,5 | 1,22 | | 1,56 | 1,20 | | ~5 |
| | 8,5 | 1,31 | | 1,56 | 1,18 | | ~2 |
| | 9,5 | 1,37 | | 1,58 | 1,12 | | ~2 |
| II a | 2,5 | 0,83 | 1,11 | | 1,58 | 0,86 | |
| | 3,5 | 0,92 | 1,16 | | 1,50 | 0.99 | |
| | 4,5 | 0.98 | 1,20 | | 1.40 | 0.98 | |
| | 6,0 | 1,07 | | 1,47 | 1,38 | | 2,50 |
| | 7,5 | 1.28 | | 1,58 | 1,33 | | 3.15 |
| | 8,5 | 1.35 | | 1,69 | 1,28 | | 3,40 |
| | 9.5 | 1,42 | | 1,76 | 1,30 | | 3,60 |
| II b | 2,5 | 0.76 | | | 1,31 | | |
| | 3,5 | 0.85 | | | 1,38 | | |
| | 4,5 | 0.90 | | | 1,39 | | |
| | 6,0 | 1.04 | | | 1,15 | | |
| | 7,5 | 1.16 | | 1,55 | 0,65 | | 0.30 |
| | 8,5 | | 1,38 | 1,62 | | 1,52 | 0.88 |
| | 9,5 | | 1,38 | 1,64 | | 1.70 | 1,18 |
| II c | 2,5 | 0.84 | 1.12 | | 2,10 | 0,28 | |
| | 3,5 | 0,83 | 1,07 | | 1.90 | 0,58 | |
| | 4,5 | 0,88 | 1,05 | | 1,80 | 0,60 | |
| | 6,0 | 1.04 | | | 1,68 | | |
| | 7,5 | 1.21 | | 1,68 | 1.68 | | 3.25 |
| | 8,5 | 1.32 | | 1,64 | 1,62 | | 3,07 |
| | 9,5 | 1,38 | | 1,68 | 1,64 | | 3.07 |
| III | 3,5 | 1,18 | | | 0,90 | | |
| | 4,5 | 1,24 | | | 0.71 | | |
| | 6,0 | 1,31 | 1,45 | | 0,15 | 0,62 | |
| | 9,5 | | 1,68 | | | ~3.0 | |
| IV | 2,5 | 0.77 | | | 1,34 | | |
| | 3,5 | 0,85 | | | 1,28 | | |
| | 4,5 | 0,94 | 1.44 | | 1,26 | | |
| | 6,0 | 1,12 | 1,43 | | 0,95 | 0,90 | |
| | 7,5 | 1,20 | 1,43 | | 0,14 | 2,10 | |
| | 8,5 | | 1,43 | | | 2,00 | |
| | 9,5 | | | | | 1,85 | |
| V a | 2,5 | 0.94 | | | 0,44 | | |
| | 4.5 | 1,09 | | | 0,37 | | |
| | 7,5 | 1,34 | | | 0,29 | | |
| V b | 2,5 | 1,09 | | | 0,18 | | |
| | 7,5 | 1,59 | | | 0,16 | | |
| Vc | 2,5 | 0,86 | | | 0,34 | | |
| | 4,5 | 0,98 | | | 0,32 | | |
| | 7,5 | 1,23 | | | 0,21 | | |

The $E_{1/2}$ values of the A and B waves of the corresponding α- and γ-quaternized pyrophthalones are quite close to the $E_{1/2}$ values of the nonquaternized pyrophthalones: the $E_{1/2}$ values of the A and B waves for II are shifted to 100 mV to the cathode side and to 90 mV, respectively, as compared with the $E_{1/2}$ values of I.

The C wave, which is not characteristic for nonquaternized pyrophthalones, begins to appear at pH 5 for the α and γ derivatives of quaternized pyrophthalones. The C wave is split in individual cases, and the overall height of this wave increases in neutral media to the four-electron level and remains virtually unchanged in alkaline media.

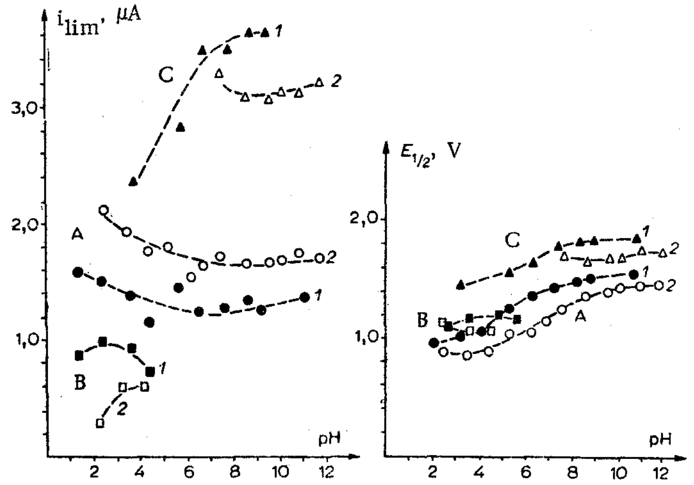


Fig. 1. Dependence of the limiting current and the half-wave potentials on the pH of the A, B, and C values for γ- (1) and α-methylpyrophthalone (2) in 20% aqueous DMF solution at a depolarizer concentration of $5 \cdot 10^{-4}$ mole/liter.

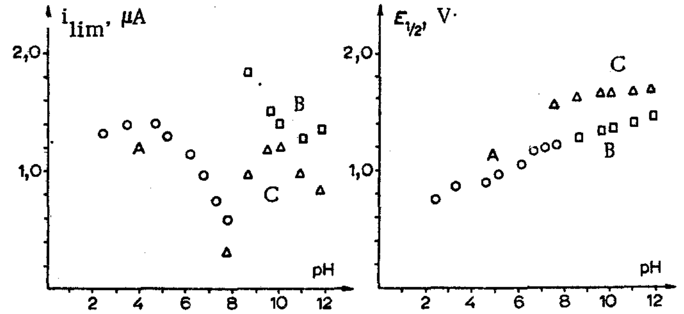


Fig. 2. Dependence of the limiting current and the half-wave potentials on the pH of the A, B, and C waves for β-methylpyrophthalone in 20% aqueous DMF solutions at a depolarizer concentration of $5 \cdot 10^{-4}$ mole/liter.

All of the nonquaternized pyrophthalones in acidic media in turn give a very high D wave (above 50 μA), but it decreases to 2 μA as the pH is increased. This wave characterizes hydrogen evolution that is catalyzed by the pyridinium base, and will not be subsequently examined in our study.

The difference between the β-pyrophthalones and the α- and γ-pyrophthalones consists primarily in the stepwise decrease in the two-electron diffusion wave A as the pH increases (Fig. 2). Moreover, IIb gives, in addition to a poorly expressed B wave, the height of which increases with the pH, a characteristic C wave at –1.65 V in alkaline media, i.e., the polarographic behavior of IIb resembles the behavior of the previously investigated 2-phenylindane-1,3-dione [5].

A study of the quaternized and nonquaternized pyrophthalones with the application of cyclical voltammetry showed that the observed peaks virtually correspond to the $E_{1/2}$ values of the waves on the classical polarograms. In addition, an anode peak with an anode peak potential ($E_a$) of –0.10 V is observed beginning at pH 6.3 only for the quaternized pyrophthalones; however, one observes this peak only in the case of scanning of the potentials up to the potential of the C wave. This peak becomes more pronounced both as the pH is increased and as the scanning rate is increased.

The character of the cyclical voltammetric curves, like the slopes of the waves, indicates the electrochemical irreversibility of all of the waves, both in the case of pyrophthalones I, and pyrophthalones II.

1-Methyl-4-(1-oxo-2-indanylidene)-1,4-dihydropyridine. A wave at −1.18 to −1.31 V, the $i_{lim}$ value of which varies with the pH in the form of a dissociation curve with $pK_{pol}$ 5.05, is characteristic for the electrical reduction of this compound in 20% aqueous DMF solutions. The decrease in this wave as the pH increases is due to a decrease in the concentration of the protonated form of III. The presence of two different protolytic forms of III was proved by the change in the UV spectrum as a function of the pH. The 1,4-dihydropyridine structure of the unprotonated form of III and protonation in the 2 position of the protonated form of III were established on the basis of the PMR spectra.

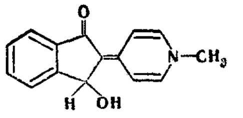
Another wave, the $E_{1/2}$ wave of which lies at −1.58 to 1.68 V, i.e., approximately at the same potentials as the C wave of γ-methylpyrophthalone IIc (Table 1), is observed in alkaline media for dihydropyridine derivative III.

The cyclical voltammetric data show that an anode peak with $E_a$ = −0.10 V is observed only in the case of scanning up to a final potential that exceeds the potential of the C wave. As in the case of pyrophthalones, the anode peak increases as the pH and scanning rate are increased.

2-phenylindane-1,3-dione. The polarographic reduction of IV in 20% aqueous DMF solution proceeds in the same way as in the case of mixed aqueous alcohol media [4, 5]; the first reduction wave of indanedione IV and the corresponding A wave of the pyrophthalones under these conditions have virtually identical potentials; however, in the case of indanedione IV this wave is reversible. The cyclical voltammetric curves [$E_a$ = +0.07 V (pH 2) and $E_a$ = −0.07 V (pH 5)] attest to electrical oxidation of the products with dienediol structures [6].

## Products of Preparative Electrolysis

Preparative electrolysis was carried out to identify the products of electrical reduction of pyrophthalone IIc in 20% aqueous DMF phosphate buffer solution. The structures of the isolated compounds were determined by PMR, UV, and mass spectroscopy. A mass-spectrometric study of the products of electrical reduction at pH 5.3 and a potential of the plateau of the limiting current of the second wave of −1.36 V showed the presence of a molecular peak with M 223 and in some cases a peak with M 239, i.e., a mixture of two compounds in which the compound with M 223 predominates was formed. Only a molecular peak with M 223 was observed in the case of the preparative electrolysis of pyrophthalone IIc at a potential of the plateau of the limiting current of the second wave at −1.20 V and pH 2.2. A 1,4-dihydropyridine structure was assigned to the indicated compounds, since the UV spectra of the electrolyzate and a solution of III are identical and contain a conjugated chromophore. By chromatographic separation of the electrolyzate we were able to isolate still more components, but we were unable to establish their structures on the base of mass-spectrometric data; profound decomposition of the molecule evidently occurred. The presence of a mixture of the indicated products of electrical reduction or decomposition products made it impossible to unambiguously interpret the PMR spectrum of the electrolyzate. On the basis of the PMR spectra one can speak only of the unsymmetrical structure of the electrical reduction product, i.e., the reduction of one of the carbonyl groups.



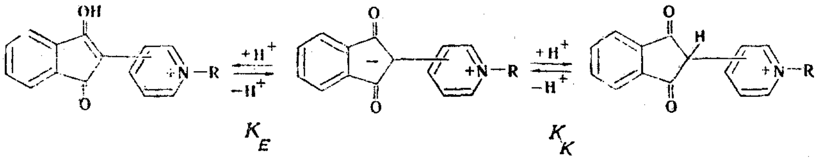
M = 239

## Protolytic Equilibria in a 20% Aqueous DMFA Britton–Robinson Buffer Solution

The percentages of the enol (α) and the overall and O- and C-acidity constants ($pK_{KE}$, $pK_E$, and $pK_K$) (Table 2) in a 20% aqueous DMF solution were determined by means of UV spectroscopy by the method in [1, 7] for I, II, and IV. The $pK_E$ and $pK_K$ values calculated from the overall acidity ($pK_{KE}$) from the Kabanchik formula [8] are in agreement with the following protolytic equilibria of the investigated pyrophthalones:

TABLE 2. Overall and O- and C-Acidity Constants and Percentages of the Enol Form of I, II, and IV in a 20% Aqueous DMF Solution

| Compound | $pK_{KE}$ | $pK_K$ | $pK_E$ | $\alpha$ |
|---|---|---|---|---|
| Ia | −2,00±0,04 | −3,15 | −2,03 | 0,93 |
| Ic | −1,02±0,02 | −2,12 | −1,05 | 0,92 |
| IIa | −0,62±0,03 | −0,79 | −1,12 | 0,32 |
| IIb | −0,01±0,11 | −0,10 | −0,74 | 0,19 |
| IIc | −1,12±0,03 | −2,04 | −1,17 | 0,88 |
| IV | 3,90±0,05 | 3,87 | 2,71 | 0,06 |



The highest percentage of the enol form ($\alpha$ = 0.93) is observed for quaternized $\alpha$-pyrophthalone IIa, while the lowest percentage ($\alpha$ = 0.19) and the lowest acidity are observed for IIb, in which the pyridinium part is not conjugated with the indanedionyl part. An even lower percentage of the enol form and an even lower acidity are characteristic for 2-phenylidane-1,3-dione, in which protonation at the carbon atom also prevents conjugation of the phenyl ring in the 2 position with the phthaloyl grouping. Acidic properties are most pronounced in the case of pyrophthalone Ia; this is due to the presence in the molecule of a strong intramolecular hydrogen bond [9]. A higher percentage of the enol form than for the $\alpha$ derivatives is always characteristic for the $\gamma$ derivatives.

From the data obtained it may be concluded that I and II (except for the $\beta$ derivatives) will primarily be reduced to the enol form on a dropping mercury electrode in acidic media, especially since the percentage of the enol form on the electrode surface exceeds the percentage in the volume of the solution, as demonstrated for 2-phenylidane-1,3-dione [5].

## Mechanism of the Electrical Reduction of Pyrophthalones in 20% Aqueous DMF Britton–Robinson Buffer Solutions

The experimental data presented above made it possible to propose a set of chemical and electrochemical reactions that are realized in the polarographic reduction of the $\alpha$ and $\gamma$ isomers of pyrophthalones I and II; this set of reactions is presented in the schemes given below. This sort of treatment is in agreement with the principles previously established for 2-phenylidane-1,3-dione [10] and also with the polarographic behavior of the model compounds.

Let us note that the schemes pertain to the $\alpha$ and $\gamma$ isomers; the electrical reduction of the $\beta$ isomer, in which the two fragments of the molecule are not conjugated with one another, is realized as in the electrical reduction of 2-phenylidane-1,3-dione at approximately the same potentials, and recombination of the enolate anion with protons evidently occurs at considerably higher pH values only in this case.

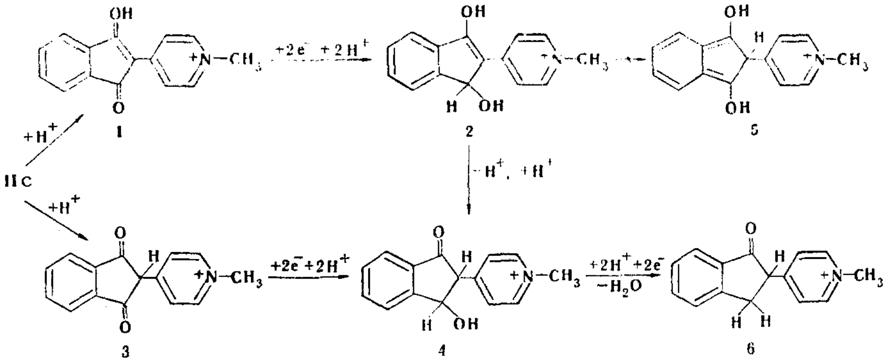


TABLE 3. Percentage of the Keto Form and Ratio of the Heights of the Waves ($i_B/i_A$) for Pyrophthalones I-II

| Compound | $1-\alpha$ | $i_B/i_A$ |
|---|---|---|
| IIa | 0,68 | 0,54 |
| IIc | 0,12 | 0,13 |
| Ia | 0,33 | 0,55 |
| Ic | 0,08 | 0,26 |

It is assumed that the protonated forms of the pyrophthalone both in enol 1 and ketone 3 forms are simultaneously involved in the first step of the electrical reduction in acidic and neutral media over the pH range in which the compounds exist in the form of a dipolar ion after prior protonation on the electrode surface.

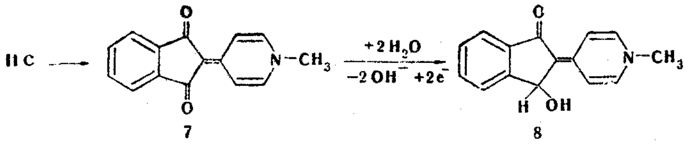
Only molecules of the indan-1-on-3-ol derivative, i.e., either molecules that are formed directly during the electrical reduction of diketo form 3 or molecules that are formed in the rearrangement of product 2, are involved in the second step of the electrical reduction. This rearrangement is proved by an increase in the B wave as the dropping period is increased. This can be explained by the fact that in the case of work with a short-period electrode ($t = 0.3$ sec) the rate of the 2→4 rearrangement is not high enough for a molecule of indan-1-on-3-ol derivative 4, which is capable of undergoing further reduction, to be formed in the lifetime of a drop during the rearrangement. As a result of this, molecules of 4 are formed only as a consequence of reduction of keto form 3, which is found in the starting solution. However, the fraction of 4 molecules increases as a result of rearrangement as the dropping period is increased. Correspondingly, the B wave also increases, reaching the height of the A wave when $t = 5$ sec. The validity of this interpretation is confirmed by the proportionality between the percentage of the keto form of the starting pyrophthalone and the height of the B wave ($i_B$) when $t = 0.3$ sec (Table 3).

The disparity between the two values for I possibly attests to partial rearrangement even during the lifetime of a drop ($t = 0.3$ sec).

We were also able to show the effect of rearrangement on the concentration of the molecules of indan-1-on-3-ol derivative 4 for IIc by means of cylical voltammetry. At low scanning rates (0.05 V/sec) for which the rearrangement has time to be realized completely, the heights of the cathode peaks of waves A and B ($i_A$ and $i_B$) are virtually identical, whereas the fraction of 4 molecules decreases at higher scanning rates, as indicated by the sharp decrease in the $i_B/i_A$ ratio.

The dependence of $i_{lim}$ of the B wave of IIc on the pH is similar to the dependence of $i_{lim}$ of the wave on the pH for III. The product of electrolysis of pyrophthalone IIc at the potential of the plateau of the limiting current of the A wave and III have identical UV spectra. This made it possible to assume that precisely the hydroxy derivative of III, which, depending on the pH, may exist in either the protonated or nonprotonated form participates in the second step of the electrical reduction of the pyrophthalones.

It should be recalled that in the case of 2-phenylindan-1,3-dione, as a result of the first step of polarographic reduction, one observes the formation of dienediol anions, protonation of which gives both dienediol molecules (which are incapable of electrical reduction but are capable of electrical oxidation) and 2-phenylindan-1-on-3-ol molecules [10]. In the electrical reduction of pyrophthalones the 2 molecules also undergo rearrangement but evidently not in the dienediol 5 form. The absence on the cyclical voltammetric curves of the anode peaks of oxidation of dienediol products that are characteristic for the electrical reduction of 2-phenylidane-1,3-dione [6] indicates the absence of a dienediol in the electrical reduction of pyrophthalones.



In alkaline media the first step of the electrical reduction is realized without prior protonation of the pyrophthalone molecule, as indicated by the absence of a dependence of $E_{1/2}$ on the pH. It may be assumed that form 7 undergoes polarographic reduction in alkaline media, since $E_{1/2}$ for pyrophthalone IIc in alkaline media is similar to $E_{1/2}$ of 2-benzylideneindane-1,3-dione ($E_{1/2} = -1.3$ V) [11]. The presence of an anode peak on the cyclical voltammetric curves with $E_a = -0.10$ V (which was also observed on the curves of model substance III in the case of a scanning potential up to the potential of the C wave of IIc) also may constitute evidence for the formation of a readily oxidizable product of electrical reduction of dihydropyridinium structure 8 in alkaline media. Electrical reduction of both the carbonyl group and the 1,4-dihydropyridine ring occurs upon further electrical reduction of indan-1-on-3-ol 8 [12], since $i_{lim}$ of the C wave reaches the four-electron level. In addition, electrical reduction in the step involving the C wave (in accordance with the scheme) is similar to electrical reduction of III in alkaline media, and this confirms the close $E_{1/2}$ values, i.e., from −1.64 to −1.68 V (for the C wave) and from −1.58 to −1.68 V (for III), as well as the presence in both cases of an anode peak with $E_a = -0.10$ V on the cyclical voltammetric curves.

## Structural Effects in the Reduction of Pyrophthalones

It follows from the experimental data and the schemes presented above that in protogenic media electrical reduction in the investigated pyrophthalones initially involves the indanedionyl part of the molecule. This is also confirmed by the close $E_{1/2}$ values of the pyrophthalones (from −0.76 to −0.84 V) and 2-phenylidane-1,3-dione (−0.77 V) at pH 2.5. At the same time, the $E_{1/2}$ values of pyridinecarboxylic acids V lie at potentials that are 100-250 mV more negative than the $E_{1/2}$ values for electrical reduction of the investigated pyrophthalones.

This sequence of the reduced groups is also substantiated by quantum-chemical calculations made by the Hückel MO method, which show that the energies of the lower vacant molecular orbitals for pyridinecarboxylic acids ($K_j = 0.0503$) are considerably higher than for pyrophthalones ($K_j = 0.0352$) and differ considerably from the energy for III ($K_j = 0.0520$). However, the presence of a pyridinium ring and its conjugation with the indanedionyl residue in the case of the α and γ isomers have a substantial effect on electrical reduction, making it different from the electrical reduction of 2-phenylindane-1,3-dione.

## EXPERIMENTAL

Compounds I-III were synthesized by the methods in [13-15].

The polarographic study of I-V was carried out in 20% aqueous DMF Britton–Robinson buffer solutions at ionic strength $\mu = 0.4$. The depolarizer concentration in all cases was $5 \cdot 10^{-4}$ mole/liter.

A PAR-170 electrochemical system (USA) and an LP-7e electronic recording polarograph (Czechoslovakian SSR) with a three-electrode circuit were used for the polarographic studies. Virtually all recordings of the classical polarograms (Table 1) were made with the latter apparatus. The working electrode was a dropping mercury electrode with forced detachment of the drops; $t = 0.5$, 1.0, 2.0, or 5.0 sec when $m = 2.16$ mg·sec$^{-1}$, or $t = 0.35$ sec when $m = 1.65$ mg·sec$^{-1}$. The anode in both cases was a platinum wire, while the reference electrode was an aqueous saturated calomel electrode. The diffusion potentials were not taken into account but were assumed to be equal in the entire series of measurements.

The millicoulometric measurements and preparative electrolysis were accomplished with a PAR-170 electrochemical system. The cyclical voltammetric curves were obtained with the same apparatus with the aid of a stationary electrode, viz., a hanging mercury drop (model 9323).

Preparative electrolysis was carried out in a 20% aqueous DMF phosphate buffer solution. To isolate the products of preparative electrolysis the solution of the electrolyzate (pH 2) was made alkaline to pH 6, and the aqueous DMF mixture was removed by distillation in a rotary evaporator. The residue was dissolved in pure DMF, and the precipitated phosphates were removed by filtration. The DMF was removed completely by distillation, and the product was dried in a vacuum desiccator.

A Varian 8500 liquid chromatograph was used for chromatographic separation of the products of preparative electrolysis. The mass-spectrometric measurements were made with an MS-50 mass spectrometer (AEI). The PMR spectra were recorded with a Bruker WH 90/DS spectrometer. The UV spectra were recorded with a Unicam SP-1800 spectrophotometer.

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