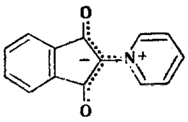
POLAROGRAPHIC STUDY OF HETEROCYCLIC YLIDS OF INDANE-1,3-DIONE

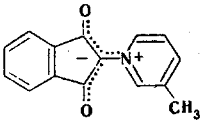
V. P. Kadysh, Ya. P. Stradyn',
Yu. A. Benders, and O. Ya. Neiland

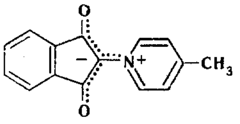
UDC 543.253:541.138.3:547.828

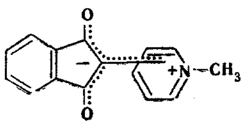
The trend of the electrochemical reduction of derivatives of 2-(N-pyridinia)-indane-1,3-dione betaines in both anhydrous dimethylformamide (DMF) and in aqueous DMF solutions was studied by classical polarography, millicoulometry, preparative electrolysis, and cyclical voltammetry. The electrical reduction of the investigated betaines in anhydrous DMF is realized through a step involving the formation of anion radicals. In aqueous DMF solutions the C—N bond undergoes cleavage during the electrical reduction to give indan-1-on-3-ol, the structure of which was established by PMR spectroscopy and mass spectrometry.

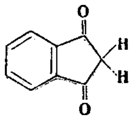
Heteroaromatic inner salts (betaines) of indane-1,3-dione (ylids I and pyrophthalones II) are of interest in view of the peculiar structure of their molecules, which contain simultaneously electron-donor and electron-acceptor components. The determination of the donor and acceptor capacities of the individual components of the molecule may provide a valuable characterization of their mutual effect in compounds of type I and II. The donor capacities (ionization potentials) were determined for a number of compounds of type I and II [1] by electron spectroscopy, whereas the acceptor capacities (electron affinities) cannot be determined by this method. It seemed to us that polarography could be used for a relative estimate of the electron affinities. In addition, the mechanism of the electrochemical reduction of compounds of type I can be established by means of polarography and related methods, and it can be compared with the mechanism previously studied for II-V.

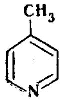

Ia

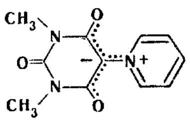

Ib


Ic


II


III


IV


V

In the present research we studied the polarographic reduction of isomeric pyridinium ylids of indane-1,3-dione (Ia-c), as well as compounds that model the individual fragments of the molecules of Ia-c, viz., indane-1,3-dione (III), γ-picoline (IV), and pyridinium barbiturate (V).

Among other things, in the course of our research we studied the problem as to whether the C—N bond between the indanedionyl and pyridinium rings undergoes cleavage during electrical reduction of the ylids. It is known that the activated C—N bond is electrochemically inert in dimethylformamide (DMF) in the absence of proton donors; however, in the presence of proton donors, especially in protogenic solvents, this sort of cleavage is possible if the structural factors also are favorable for this [2]. We therefore made a systematic study of Ia-c in anhydrous DMF, in anhydrous DMF with the addition of proton donors (phenol and benzoic acid), in 10, 20, 30, and 40% aqueous DMF Britton—Robinson buffer solutions, and in a 20% aqueous DMF 1 M solution of H_2SO_4. In the last of the media cited we studied the polarographic behavior of II, III, and V for comparison.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 369-375, March, 1980. Original article submitted July 13, 1979.

0009-3122/80/1603-0278$07.50

TABLE 1. Half-Wave Potentials ($E_{1/2}$) and Limiting Currents (i_{lim}) for Pyridinium Ylids of Indane-1,3-dione in Dimethylformamide with 0.1 N Tetrabutylammonium Perchlorate as the Base Electrolyte

Compound	First wave		Second wave	
	$-E_{1/2}$, V	i_{lim}, μA	$-E_{1/2}$, V	i_{lim}, μA
Ia	1,47	1,3	2,27	1,35
Ib	1,49	1,15	2,28	1,45
Ic	1,54	1,10	2,26	1,30
V	1,38	1,70	—	—

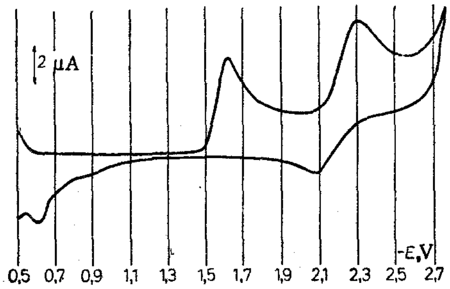


Fig. 1. Cyclical volt—ampere curves of 4-methyl-2-(N-pyridinia)-indane-1,3-dione betaine (Ic) in DMF with 0.1 N tetrabutylammonium perchlorate as the base electrolyte (the scanning rate was 1 V/sec, the polarization ranged from −0.5 to −2.7 V, and the depolarizer concentration was $5 \cdot 10^{-4}$ mole/liter).

Electrical Reduction in an Aprotic Medium

Compounds Ia-c give two polarographic waves in anhydrous DMF (Table 1). The numbers of electrons consumed in the first step of the electrical reduction of Ib,c determined by millicoulometry were 0.89 and 1.35, respectively, whereas the values calculated from the Ilkovic equation were 0.93 and 0.98, i.e., the first polarographic waves are one-electron waves. From a comparison of the i_{lim} values of the first waves of Ia and Ib it may be concluded that in the case of Ia the first step in the electrochemical reduction is a one-electron step.

It is apparent from the data from cyclical voltammetry that the first wave of Ia-c is completely irreversible (over a range of change in the scanning rates of 0.1-1.0 V/sec) (Fig. 1). An anode peak corresponding to the first cathode peak is completely absent; however, in return an anode peak appears over a considerably more positive range of potentials (from −0.6 to −0.7 V). As in the case of 2-pyridylindane-1,3-diones [3], prolonged electrolysis at the potential of the plateau of the limiting current of the first wave leads to the appearance in time of an additional wave of electrical oxidation over the same range of potentials (−0.6 to −0.7 V).

The EPR spectra recorded for Ia,c in an experiment in a cell for electrochemical generation of radicals at the potentials of the plateau of the limiting current of the first wave prove the formation of free anion radicals. The hyperfine structures (hfs) of the EPR spectra of both indane-1,3-dione derivatives [4] and pyrophthalone derivatives [5] is a triplet with a ratio of the intensities of the individual components of 1:2:1 and an hfs constant of 2 Oe, i.e., the unpaired electron is localized in the 5 and 6 positions of the phthaloyl ring. Thus the first step of the electrochemical reduction in DMF in the case of Ia-c involves the entire conjugated system.

However, in the case of those pyridinium betaines the negative fragment of the molecule of which is not capable of electrical reduction (V), the pyridinium ring is reduced

TABLE 2. Half-Wave Potentials ($E_{1/2}$) and Limiting Currents (i_{lim}) for Pyridinium Ylids of Indane-1,3-dione in a 20% Aqueous Dimethylformamide Solution of 1 M H_2SO_4 with 0.1 N Tetrabutylammonium Bromide as the Base Electrolyte

Compound	First wave		Second wave	
	$-E_{1/2}$, V	i_{lim}, μA	$-E_{1/2}$, V	i_{lim}, μA
Ia	0,63	1,52	0,90	0,87
Ib	0,64	1,47	0,90	1,15
Ic	0,61	1,55	0,92	1,55
II (γ- pyrophthalone)	0,65	—*	—	—
III	0,68	1,50	—	—
IV	—	—	—	—

*The i_{lim} value of the wave of γ-pyrophthalone is not presented, since, because of its limited solubility, the concentration of the polarographic solution is lower than $5 \cdot 10^{-4}$ mole/liter.

at −1.38 V; the anionic barbiturate part hinders electrical reduction to the extent of 160 mV as compared with the quaternary methylpyridinium salt [3].

The second wave of Ia-c has a height that is approximately equal to the height of the first wave. The cathode peaks on the cyclical voltammetric curves that correspond to it have an anode branch (Fig. 1); however, the difference between the potentials of the cathode (E_c) and anode (E_a) peaks is considerably greater than in the case of a strictly reversible process, and, in addition, the form of these peaks is somewhat distorted during the subsequent cycles, and new, small, and poorly expressed peaks appear, i.e., the electrode process is distorted by side processes during the reduction of these compounds on a stationary mercury electrode. It should be assumed that as in the case of 2-phenylindane-1,3-dione, dienediols are formed and subsequently undergo disproportionation [6].

The effect of the addition of proton donors to DMF solutions of Ia-c is identical to the effect observed in the case of pyrophthalones. Phenol added in a concentration that exceeds the concentration of the substance under investigation by one order of magnitude does not affect the $E_{1/2}$ and i_{lim} values of the first wave; however, the height of the second wave increases by a factor of 1.52, and the $E_{1/2}$ values undergo an approximately 200 mV shift to the positive side. Benzoic acid, being a stronger proton donor, increases both the first and second waves by a factor of approximately two with an attendant 100 mV shift of the $E_{1/2}$ values to the positive side.

Thus, the polarographic behavior of pyrophthalones and ylids is very similar, at least in the first step, on the basis of which it may be concluded that in anhydrous DMF the C—N bond in the ylids does not undergo cleavage in either the first or second step of the electrical reduction.

As compared with α-, β-, and γ-pyrophthalones [3], pyridinium ylids are reduced more easily (by 200-250 mV) in DMF, and this indicates the effect of the direct proximity of the positively charged pyridinium nitrogen atom with respect to the negative phthaloyl fragment. This, by the way, is also evidence in favor of the fact that electrical reduction involves primarily the phthaloyl fragment.

Reduction in Protogenic Media

In an acidic medium (a 20% aqueous DMF solution of 1 M H_2SO_4) Ia-c give two well expressed polarographic waves with approximately identical heights (Table 2); whereas the first wave of Ia-c is close to the corresponding wave of indane-1,3-dione with respect to the $E_{1/2}$ and i_{lim} values, the second wave is distinctly expressed only in the case of the ylids. In the case of indane-1,3-dione, which is reduced at a potential that is on the average 50 mV more negative than in the case of Ia-c, as a consequence of the absence of an acceptor, viz., the pyridinium fragment, the second wave, just as in the case of γ-pyrophthalone, is completely absent. Under these conditions γ-picoline is not polarographically active.

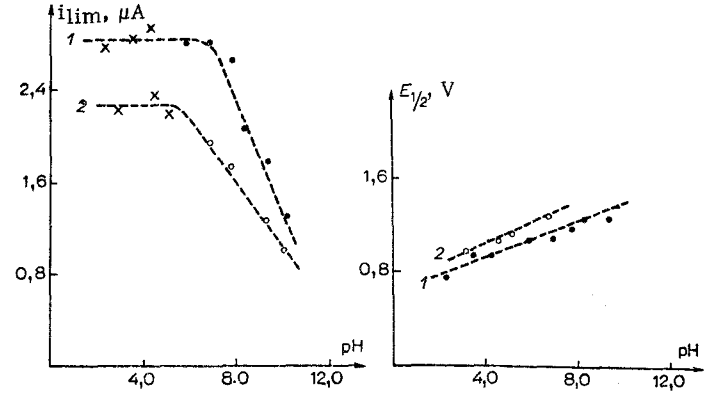


Fig. 2. Dependence of the limiting current (i_{lim}) and the half-wave potentials ($E_{1/2}$) on the pH for 4-methyl-2-(N-pyridinia)indane-1,3-dione betaine (Ic) in 10% (1) and 40% (2) aqueous DMF Britton–Robinson buffer solutions (× is the overall value of the first and second waves. The depolarizer concentration was $5 \cdot 10^{-4}$ mole/liter.).

The numbers of electrons consumed in the first step of the electrochemical reduction were calculated from the Ilkovic equation and were found to be 1.90, 1.83, and 1.93 for ylids Ia,b,c, respectively. To verify the correctness of the calculation for ylid Ic the number of electrons was also determined by a millicoulometric method. It was found to be 2.25. Taking into account the approximate equality of the limiting currents of the first and second waves, we concluded that the second wave is also a two-electron wave.

The investigated compounds in a protogenic medium are reduced after prior protonation, which may proceed at both the carbon and oxygen atoms to give a mixture of C- and O-protonation products. In order to ascertain the predominant form in which compounds of type I exist in solution, we used UV spectrometry to determine the percentage of the enol (α) and the acidity constants of the keto-enol mixture (pK_{KE}) in a 20% aqueous DMF solution. The tautomeric equilibrium constants (K_T) and the acidity constants of the ketone (pK_K) and enol (pK_E) forms [7] were calculated from the Kabachnik formula. For ylid Ic they were found to be as follows: $\alpha = 0.04$, $pK_{KE} = -0.58$, $pK_K = -0.60$, $pK_E = -1.99$, and $K_T = 0.04$. However, considering the fact that the oxygen atom primarily is protonated on the electrode surface in the case of 2-phenylindane-1,3-dione [6], one cannot exclude the possibility that the enol form that is produced as a result of prior surface protonation undergoes reduction in the first step in this case also.

To prove the assumption that the second wave of the ylids corresponds to reductive cleavage of the C–N bond between the indanedionyl and pyridinium rings, we carried out controllable potential electrolysis at the potential of the plateau of the limiting current of the second wave (−0.93 V) in 1 M HCl.* The final electrolysis product, the PMR spectrum of which corresponds to the spectrum of unsubstituted indan-1-on-3-ol, was isolated. This structure is also confirmed by the molecular peak with M = 148 in the mass spectrum. We were unable to identify the pyridinium part of the molecule by the methods indicated above or by gas–liquid chromatography. The pyridine derivatives (picolines) are lost in the process of isolation of the final product from the electrolyzate, evidently because of their volatility.

In examining the problem as to whether the C–N bond undergoes cleavage only at high acidities of the medium or in moderately acidic media we made a polarographic study of the ylids in 20% aqueous DMF Britton–Robinson buffer solutions at pH 2-11. To ascertain the effect of the DMF concentration on the overall trend of the reduction we also made similar studies in 10, 20, 30, and 40% aqueous DMF solutions.

The pattern of the polarographic reduction of ylids Ib and Ic in Britton–Robinson buffer solutions is complex (Fig. 2). In acidic media (pH 2) they give two polarographic

---

*When controllable potential electrolysis is carried out, the 1 M H_2SO_4 must be replaced by 1 M HCl, since H_2SO_4 hinders removal of the water from the electrolyzate by distillation.

waves with approximately equal heights that as the pH is increased merge into one wave, the height of which decreases uniformly until it vanishes completely at pH > 10. A new wave that increases as the pH increases appears simultaneously at pH > 6. A similar pattern is observed in aqueous DMF solutions of all four concentrations if one does not take into account the fact that the limiting currents change somewhat because of a change in the viscosity of the aqueous DMF solutions [8], and the $E_{1/2}$ values of all three waves are shifted 60-80 mV as the DMF concentration is increased from 10 to 40% (by volume).

Since the initial two waves merge very rapidly into one and are difficult to separate even at pH 2.0 because of the close $E_{1/2}$ values, the numbers of electrons were calculated from the Ilkovic equation for the overall wave and were found to be close to four (values of 3.84, 3.24, 3.74, and 3.95 were found for imide Ib in the case of 10, 20, 30, and 40% aqueous DMF Britton–Robinson solutions respectively).

For controllable potential electrolysis we selected a pH value of 5.2, i.e., the limiting pH value at which the overall current of the first two waves still remains constant (Fig. 2); however, it was necessary to replace the Britton–Robinson buffer solution by a simpler (in composition) phosphate buffer solution with the same pH value. Controllable potential electrolysis was carried out at the plateau of the limiting current of the second wave (−1.1 V). As in the case of 1 M HCl, the PMR spectrum of the reaction product corresponds to the spectrum of indan-1-on-3-ol, and this constitutes evidence for cleavage of the C–N bond under these conditions also, i.e., in media that are close to neutral.

Considering the pK_{KE} values of I (~ -0.6) it may be assumed that the electrochemical cleavage of the C–N bond is realized either in the cationic form of the starting molecule (with allowance for the possibility of protonation on the electrode surface) or in the product formed after the addition of two electrons [i.e., in 2-(N-pyridinia)-indan-1-on-3-ol], which overall gives a four-electron polarographic wave. At higher pH values, where Ia-c exist in the form of a dipolar ion or anion, ylids I are not protonated, the C–N bond does not undergo cleavage, and only the indane-1,3-dionyl part of the molecule undergoes reduction, as in the case of unsubstituted indane-1,3-dione [9]. The pyridinium part of the molecule is not reduced at the accessible potentials because of the effect of the negative part of the molecule.

Thus, the acceptor rather than the donor fragment of the molecule is reduced on the electrode in the electrochemical reduction of ylids of indane-1,3-dione.

If, however, the pyridinium betaine does not contain an electrically active anionic donor grouping, the acceptor fragment (the pyridinium part) is reduced, as in the case of V (barbituric acids are not reduced on a dropping mercury electrode).

EXPERIMENTAL

Compounds Ia-c were synthesized by a previously described method [10], and their purity was monitored from their melting points.

The polarographic study was carried out in anhydrous DMF (the inert electrolyte was tetrabutylammonium perchlorate with an ionic strength of 0.1) in 10, 20, 30, and 40% aqueous DMF Britton–Robinson buffer solutions and in a 20% aqueous DMF 1 M H_2SO_4 solution (the inert electrolyte was tetrabutylammonium bromide with an ionic strength of 0.1). The depolarizer concentration in all cases was $5 \cdot 10^{-4}$ mole/liter. A PAR-170 (U.S.A) electrochemical system and an LP-7e electronic recording polarograph (Czechoslovakian SSR) involving a three-electrode scheme were used. A dropping mercury electrode with forced detachment of the drops and either $t = 0.5$ sec and $m = 2.16$ mg-sec^{-1} or $t = 0.35$ sec and $m = 1.65$ mg-sec^{-1} served as the working electrode. A platinum wire served as the anode in both cases, and an aqueous saturated calomel electrode served as the reference electrode. The millicoulometric measurements and controllable potential electrolysis were realized with a PAR-170 electrochemical system. The cyclical volt–ampere curves were obtained with a stationary electrode, viz., a hanging mercury drop (model 9323) with a surface area of 2.87 mm^2. The diffusion coefficients (D) necessary for the calculation of n from the Ilkovic equation were estimated from the Stokes–Einstein equation [the density of the pure substance (1.47 [11]) was found by an x-ray diffraction method for Ia and was adopted in our calculations for all of the investigated ylids). In the case of the calculation of the n values in aqueous DMF Britton–Robinson solutions the change in the viscosity of the latter was taken into account; the D values were found to be $6.81 \cdot 10^{-6}$ cm^2-sec^{-1} in anhydrous DMF and $3.92 \cdot 10^{-6}$, $3.18 \cdot 10^{-6}$, $2.58 \cdot 10^{-6}$, and $2.14 \cdot 10^{-6}$ cm^2-sec^{-1} in 10, 20, 30, and 40% aqueous DMF solutions, respectively.

Methods for Isolation of the Final Product of Electrolysis. After controllable potential electrolysis in a 20% aqueous DMF solution of 1 M HCl, the electrolyzate was made alkaline with concentrated sodium hydroxide solution for neutralization of the HCl. The water and DMF were removed from the neutralized solution by distillation in a rotary evaporator. The residue obtained was dissolved in distilled water until the resulting NaCl dissolved completely in it, and the precipitated final product was removed by filtration and dried in a vacuum desiccator.

When controllable potential electrolysis was carried out in a 20% aqueous DMF phosphate buffer solution, the electrolyzate obtained was distilled in a rotary evaporator up to the point of complete removal of the aqueous DMF mixture. Pure DMF was added to the residue to dissolve the final product of electrolysis, and the precipitated phosphates were separated by centrifugation. The DMF solution containing the product was distilled in a rotary evaporator up to the point of complete removal of the DMF, and the residual product was dried in a vacuum evaporator.

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. PMR spectrum of the final product of the electrolysis of indan-1-on-3-ol ($CDCl_3$), δ: 7.8-7.4 (4H, m, C_6H_4), 5.4 (1H, dd, J = 6.4 and 3.0 Hz, H_3), 3.10 (1H, dd, J = 6.4 and 18.6 Hz, H_2), 2.60 (1H, dd, J = 3.0 and 18.6 Hz, H_2), and 2.1 ppm (1H, s, OH).

We thank our senior scientific co-worker É. É. Liepin'sh for interpretation of the PMR spectra.

LITERATURE CITED

1. V. É. Kampar and O. Ya. Neiland, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 6, 727 (1975).
2. J. Stradins and V. Vegnere, Bioelectrochem. Bioenerg., No. 4, 195 (1977).
3. Ya. P. Stradyn', V. P. Kadysh, L. M. Baider, É. S. Lavrinovich, and Yu. É. Fridmanis, Khim. Geterotsikl. Soedin., No. 8, 1097 (1977).
4. J. Benders, L. Baumane, R. Gavars, and J. Stradins, J. Mol. Struct., 19, 431 (1973).
5. Ya. P. Stradyn', Yu. Benders, V. P. Kadysh, É. S. Lavrinovich, and Yu. É. Fridmanis, Khim. Geterotsikl. Soedin., No. 2, 218 (1980).
6. Ya. P. Stradyn' and V. P. Kadysh, Coll. Czech. Chem. Commun., 36, 698 (1971).
7. M. I. Kabachnik, Dokl. Akad. Nauk SSSR, 83, 859 (1952).
8. A. Fratiello, J. Mol. Phys., 7, 565 (1964).
9. O. Ya. Neiland, Ya. P. Stradyn', É. A. Silin'sh, et al., Structure and Tautomeric Transformations of β-Dicarbonyl Compounds [in Russian], Zinatne, Riga (1977), p. 236.
10. I. K. Raiskuma, G. G. Pukitis, and O. Ya. Neiland, Khim. Geterotsikl. Soedin., No. 7, 889 (1978).
11. S. K. Apinitis and O. Ya. Neiland, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 1, 37 (1975).