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POLAROGRAPHY OF 5-ARYLFURFURALS IN AQUEOUS ALCOHOL MEDIA

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The reduction of 5-arylfurfurals on a dropping mercury electrode in aqueous alcohol media proceeds via the same mechanism as the reduction of unsubstituted furfural; the reduction wave of the anion radical of 5-arylfurfurals was detected for the first time. The $E_{1/2}$ values correlate with the σ constants of the substituents in the para position of the phenyl ring, and the correlation coefficient depends on the pH of the medium; this is determined by the different contributions of the protonation reactions after transfer of the first electron for compounds of the investigated series.

Of the rather large number of papers devoted to the polarographic study of furfural and its derivatives, the mechanism of the reduction of furfural on a dropping mercury electrode has been examined in greatest detail in [1-3], in which it was established that carbonyl compounds of the furan series are reduced in aqueous alcohol buffer media in conformity with the principles established for aromatic carbonyl compounds [4].

In order to study the effect of an aryl substituent, in the present research we investigated the reduction of 5-(p-R-phenyl)furfurals (R = Cl, Br, H, OCH_3, and CH_3) on a dropping mercury electrode in 50% aqueous ethanol buffered and unbuffered media.

One polarographic wave, the height of which corresponds to transfer of one electron, is observed in strongly acidic solutions at pH < 2 for all of the compounds. In this case the second wave is hidden by the discharge current of the base electrolyte. At pH 3-7 the polarograms contain two one-electron reduction waves. As in the case of furfural [1], the first wave is shifted to negative potentials as the pH increases, while $E_{1/2}$ of the second wave is independent of the pH. This leads to merging of both waves at pH 7 to give one two-electron reduction wave.

At pH 9-14 the two-electron wave is halved (Fig. 1). Thus in the reduction of 5-arylfurfurals in acidic media the protonation step precedes the electrode reaction, and the ketyl radical formed in the first step is reduced with greater difficulty than the protonated complex of 5-arylfurfurals. In addition, the electron affinity of the ketyl radical is higher than that of the starting depolarizer, and the second wave of 5-arylfurfurals in acidic media is therefore found at higher positive potentials than the two-electron wave due to the reduction of 5-arylfurfurals in the unprotonated form (Fig. 2).

Just as in the case of furfural, the $E_{1/2}$ value of the starting depolarizer is −1.35 V, whereas the $E_{1/2}$ value of the corresponding ketyl radical is −1.30 V [3].

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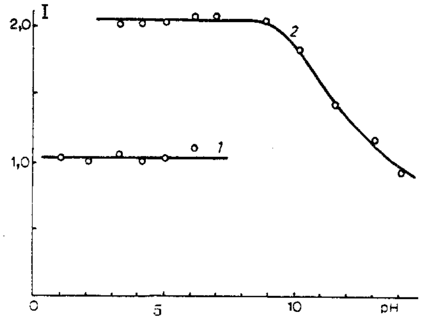

Fig. 1

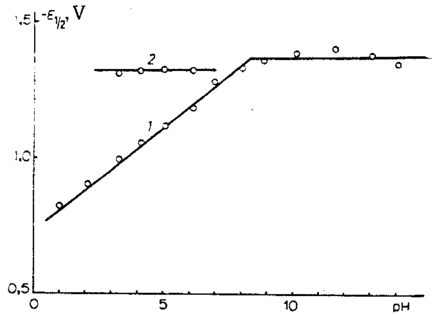

Fig. 2

Fig. 1. Dependence of the limiting current constant $I = (i/c)m^{2/3}t^{1/6}$ of 5-phenylfurfural on the pH of the medium: 1) first wave; 2) overall reduction process.

Fig. 2. Dependence of the $E_{1/2}$ value of 5-phenylfurfural on the pH: 1) first wave; 2) second wave.

The two-electron wave of the reduction of 5-arylfurfurals corresponds to an ECE mechanism with a fast ring involving protonation of the intermediately formed anion radical. An increase in the pH leads to a decrease in the rate of the intermediate chemical step, as a result of which the height of the wave decreases to the level corresponding to transfer of one electron.

In buffered media the wave of reduction of the anion radicals is hidden by the discharge current of the base electrolyte, but when unbuffered KCl solutions were used in the case of 5-phenylfurfural and its p-Cl and p-Br derivatives, i.e., compounds with electron-acceptor substituents, we were unable to record two reduction waves (Fig. 3). Under these conditions the second wave can be ascribed to reduction of the anion radicals. In fact, the first reduction wave lies at the same potentials as the two-electron wave of reduction of 5-arylfurfural in buffered solutions with pH 7-9. Since the only proton donor in unbuffered KCl solutions is water, the rate of protonation of the anion radicals is lower than in buffered media, and the reduction wave does not reach the level corresponding to transfer of two electrons. The difference between the height of this wave and the height of the wave corresponding to the one-electron process is the kinetic current limited by the rate of protonation of the anion radicals under the influence of water. As in the reduction of furfural [3], this reaction evidently is a volume reaction. In this case, as the current increases, the pH of the near-electrode space increases, and this leads to a decrease in the thickness of the reaction layer and a decrease in the rate of formation of ketyl radicals. In conformity with this, the kinetic component of the first wave of reduction of 5-arylfurfurals in unbuffered media is a nonlinear function of the depolarizer concentration – the higher the depolarizer concentration, the smaller the fraction of the kinetic component of the overall current. In addition, the theoretical relationship between the magnitude of the kinetic current and the depolarizer concentration [5] is not observed in this case, probably in connection with the fact that the limiting kinetic current constitutes a considerable fraction of the diffusion current.

The sum of the two waves of reduction of arylfurfurals in unbuffered media corresponds to transfer of two electrons. As in the case of furfural [1], the first wave is apparently partially reversible and is therefore shifted slightly to positive potentials as the ionic strength of the solution increases (Fig. 3), while $\Delta E_{1/2}/\Delta \log \mu$ for the second wave exceeds the change in the ψ' potential.* This effect of the ionic strength of the medium is characteristic for the reduction of anions [6]. The conclusion that the second wave corresponds to the reduction of ketyl anion radicals is also confirmed by experiments involving the method of latent limiting currents [7]. The development of a new wave at more positive potentials (wave A, Fig. 4) and a decrease in the wave of reduction of the ketyl anion radicals are observed when strong acid is added to a 0.1 M KCl solution containing 50% ethanol and 1.05 mM 5-(p-bromophenyl)furfural. When there are insufficient hydronium ions to enable all of the depolarizer in the near-electrode layer to form a complex with a proton, the limiting current of wave A depends on the acid concentration and is less than half of the overall current (curve 2, Fig. 4). As the acid concentration is increased further, wave A reaches half the overall limiting current, i.e., it corresponds to transfer of one electron, and its height no longer depends on the hydronium ion concentration, although $E_{1/2}$ is shifted somewhat to the positive potential region. In this case wave A corresponds to the process

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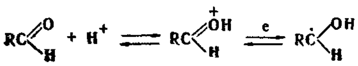
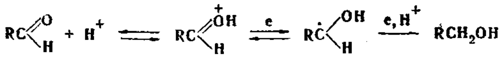
*In alkaline media, in which the wave corresponds to transfer of one electron, $\Delta E_{1/2}$ amounts to only 30 mV on passing from 0.1 M to 1 M NaOH solutions.



$$\mathrm{RC}\langle{}^{O}_{H} + H^+ \rightleftharpoons \mathrm{RC}\langle{}^{\overset{+}{O}H}_{H} \xrightleftharpoons{e} \mathrm{R\dot{C}}\langle{}^{OH}_{H}$$

In the case of excess proton donors, in addition to wave A, one also observes on the polarograms wave B (with a height equal to that of wave A) and a wave of reduction of hydronium ions (curve 4, Fig. 4). Wave B corresponds to discharge of the ketyl radicals. This can be judged from the equality of the $E_{1/2}$ values of wave B and the second wave of reduction of 5-(p-bromophenyl)furfural in acidic buffered media. In addition, wave B lies in the region of more positive potentials than the wave of reduction of the unprotonated form of the starting depolarizer (compare curves 1 and 4, Fig. 4). The processes taking place at the potentials of wave B can be represented by the scheme



$$\mathrm{RC}\langle{}^{O}_{H} + H^+ \rightleftharpoons \mathrm{RC}\langle{}^{\overset{+}{O}H}_{H} \xrightleftharpoons{e} \mathrm{R\dot{C}}\langle{}^{OH}_{H} \xrightarrow{e,H^+} \mathrm{RCH_2OH}$$

The appearance of wave B only after wave A reaches a maximum height (curve 3, Fig. 4) is explained by the fact that at the potentials of wave A the reduction of arylfurfurals is accompanied by the consumption of one proton, whereas at the potentials of wave B it is accompanied by the consumption of two protons. Thus, when the diffusion current of the hydronium ions to the surface of the electrode is smaller than required for transfer of one proton, wave B is not visible ("hidden current"), since transfer from one-electron to two-electron reduction with the consumption of two protons occurs when the potentials of wave B are reached. In this case, in addition to wave A, one observes a wave of reduction of the residual unprotonated depolarizer and the anion radical of 5-(p-bromophenyl)furfural. Wave B (curve 3, Fig. 4), which increases as the acid concentration is further increased, develops on the polarograms of 5-(p-bromophenyl)furfural only when the hydronium ion concentration in the near-electrode layer becomes higher than required for transfer of one proton. In this case the waves of reduction of the unprotonated depolarizer and the ketyl anion radicals decrease.

Thus, 5-arylfurfurals are reduced on a dropping mercury electrode in the same way as furfural; for this class of compounds we have been able, apparently for the first time, to record a wave of reduction of ketyl anion radicals in aqueous alcohol media.

Previously in [8] on the basis of a polarographic study of 5-substituted 2-nitrofurans and p-substituted nitrobenzenes it was shown that the conductivity of the polar effect of a substituent through the furan ring is higher by a factor of 1.1 than through the benzene ring. According to the PMR spectral data [9], this value is 1.2. On the other hand, it was established in [10, 11] that the transmission factor (π') of the furan ring depends markedly on the solvent and is substantially larger than the value of the benzene ring. Beno and co-workers [12] arrived at the same conclusion by an analysis of the polarographic reductions of m- and p-substituted 5-arylfurfurals in aqueous alcohol buffered media ($\pi' = 0.61$, i.e., it exceeds the π' value of the benzene ring by a factor of two). The $E_{1/2}$ values, measured in a 50% aqueous buffer solution with pH 12, were used in this paper for the construction of the correlation dependence, during which it was noted that the ρ value decreases as the pH decreases and that at pH ~ 2.5, at which the investigated aldehydes form one one-electron wave, the r value is found on the boundary of the statistical significance. This character of the dependence of the ρ value on the pH is most likely associated with the different contributions of the protolytic reactions for compounds of the investigated series. In our opinion, the choice of pH 12 for the construction of the correlation dependence in [12] was unfortunate, since at this pH the height of the wave is higher than the level corresponding to transfer of one electron, i.e., the ketyl anion radical obtained by transfer of one electron is still capable of undergoing partial protonation and takes on an electron at the same potentials. The contributions of this process for compounds of the given series may differ. In fact, the "polarographic" pK_a values of the ketyl anion radicals that we obtained, i.e., the pH values at which the height of the two-electron wave decreases by one fourth (or, correspondingly, the kinetic wave current due to protonation of the ketyl anion radicals amounts to half the diffusion current, when the rate of protonation is not the rate-determining step in the process) were found to be 11.1 for 5-phenylfurfural, 10.5 for the p-Cl derivative, 10.5 for the p-Br derivative, 10.8 for the p-CH_3 derivative, and 10.4 for the p-OCH_3 derivative. According to our data, the ρ value also depends on the pH, and the maximum ρ value is observed when the increase in the wave above the level corresponding to the transfer of one electron has pronounced kinetic character, i.e., at pH 11-12.* On passing to a 0.1 M NaOH solution the rate of protonation of the ketyl anion-radicals of 5-arylfurfurals becomes so low that the polarographic wave corresponds to the transfer of one electron. In this case the ρ value decreases and remains constant as the NaOH concentration increases.

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*The parameters of the correlation equation that we obtained at pH 11.6 [$E_{1/2}{}^0 = -1.405$ V, $\rho = 0.169$, and $s_0 = 0.004$ ($P = 0.95$)] are close to the parameters presented in [12] for pH 12 [$E_{1/2}{}^0 = -1.420$ V, $\rho = 0.179$, and $s_0 = 0.003$].

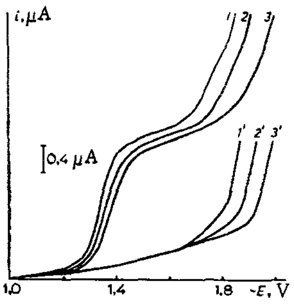

Fig. 3

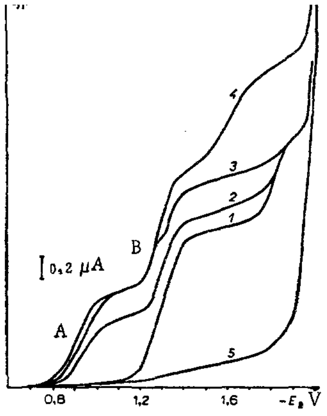

Fig. 4

Fig. 3. Polarograms of a 0.52 mM solution of 5-(p-chlorophenyl)-furfural in 50% aqueous ethanol at various concentrations of the base electrolyte (KCl): 1) 0.01 M; 2) 0.1 M; 3) 1.0 M (curves 1', 2', and 3' were recorded for the corresponding base electrolyte solutions).

Fig. 4. Polarograms of 1.05 mM 5-(p-bromophenyl)furfural in a 0.1 M solution of KCl in 50% aqueous ethanol (base electrolyte) in the presence of various concentrations of HCl: 1) c = 0; 2) c = 0.50 mM; 3) c = 0.83 mM; 4) c = 1.48 mM HCl; 5) curve of the base electrolyte current.

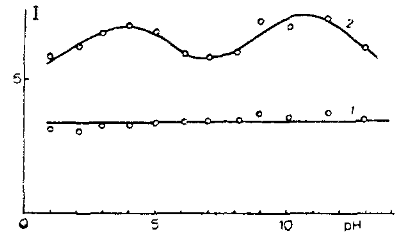

Fig. 5

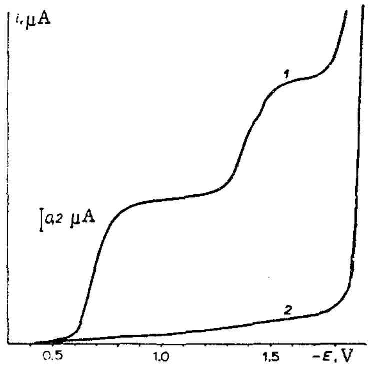

Fig. 6

Fig. 5. Dependence of the limiting current constant $I = (i/c)m^{2/3} \cdot t^{1/6}$ of 5-(p-nitrophenyl)furfural on the pH of the medium: 1) first wave; 2) overall reduction process.

Fig. 6. Polarogram of a 0.49 mM solution of 5-(p-nitrophenyl)-furfural (1) in a 0.1 M NaOH base electrolyte in a 50% aqueous methanol medium (2).

Thus one should more likely use the π' values calculated from the $E_{1/2}$ values in 0.1 M NaOH solution for the calculation of the ρ value of the furan ring from the component of the ρ values for substituted 5-arylfurfurals and substituted benzaldehydes; however, in this case also the different contributions of the subsequent chemical steps may affect the $E_{1/2}$ values, since, according to cyclic voltamperometry data, the anion radicals of 5-arylfurfurals are unstable and can be observed only at potential imposition rates higher than 1 V/sec.

5-(p-Nitrophenyl)furfural. The polarographic reduction of 5-(p-nitrophenyl)furfural presents a more complex picture, since in this case, in addition to the waves of reduction of the aldehyde group, waves of reduction of the nitro group are present.

The overall picture of the reduction is close to the behavior, described in [13], of 5-nitrofurfural on a dropping mercury electrode. Depending on the pH, the overall number of electrons consumed in the reduction of 5-(p-nitrophenyl)furfural ranges between seven and eight. Over the entire investigated pH region (1-13) the first four-electron wave corresponds to the reduction of the NO_2 group with the formation of a hydroxylamine derivative. In strongly acidic media (pH < 2) the second wave corresponds to transfer of two electrons to the protonated hydroxylamine group, i.e., it undergoes reduction to a NH_2 group. In this case, as in the reduction of 5-phenylfurfural, one observes only a one-electron wave of the aldehyde group, and the total number of electrons consumed is therefore seven. Despite the fact that there is a phenyl ring between the nitro group and the furan ring, transfer of electrons also to the unprotonated NHOH group is evidently possible, as in the case of 5-nitrofurfural. Therefore, although the height of the second wave falls to zero at pH > 2, at more negative potentials one observes the development of a wave of reduction of the unprotonated hydroxylamino group, which is overlapped with the wave of reduction of the aldehyde group. Over this pH range a wave of reduction of the ketyl radicals also appears, and the overall limiting current reaches a level corresponding to the transfer of eight electrons. Over the medium pH range (Fig. 5), the decrease in the total limiting current is evidently due to hydration of the carbonyl group, and, as in the case of 5-nitrofurfural, splitting of the first wave of reduction of the nitro group, because of the fact that the gem-diol group has considerably less pronounced electron-acceptor properties, is observed at these pH values. The decrease in the overall current in the alkaline region is associated, as in the reduction of 5-arylfurfurals, with a decrease in the rate of protonation of the ketyl anion radicals. Three waves (Fig. 6), the first of which corresponds to four-electron reduction of the nitro group, the second of which corresponds to two-electron reduction of the hydroxylamino group, and the third of which corresponds to one-electron reduction of the aldehyde group, are observed for 5-(p-nitrophenyl)furfural in a 0.1 M NaOH base electrolyte. Both the ratio of the waves and the $E_{1/2}$ value of the third wave (−1.480 V) provide evidence for this. In fact, calculation of the $E_{1/2}$ value for 5-(p-aminophenyl)furfural in a 0.1 M NaOH base electrolyte from the correlation equation $E_{1/2} = -1.381 + 0.139\sigma$, obtained from the $E_{1/2}$ values of 5-(p-R-phenyl)furfural in a 0.1 M NaOH base electrolyte, leads to −1.472 V.

EXPERIMENTAL

A capillary with a blade for forced detachment of drops was used in the present research; the characteristics were as follows: $m = 1.06$ mg, $t = 0.305$ sec, and $m^{2/3}t^{1/6} = 0.85$. An external calomel electrode served as the anode. The experiments were carried out in a thermostated cell at 25 ± 0.1°. The oxygen was removed from the solutions undergoing polarography with a stream of dry nitrogen. The polarograms were recorded with a Radiometer PO-4 polarograph.

Citrate-phosphate and phosphate buffer solutions, the pH values of which were monitored by a Radiometer PHM22T pH-meter, were used in this study.

The methods for the preparation and purification of the investigated 5-arylfurfurals are presented in [14, 15].

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