POLAROGRAPHIC BEHAVIOR OF 2, 2'-BIFURYL AND 2, 2'-FUROIN

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In aqueous and aqueous-ethanolic buffer solutions at pH<9, 2,2'-bifuryl and 2,2'-furoin give two-electron polarographic electroreduction waves, the half-wave potentials of which depend on the pH. The primary product of the electroreduction of 2,2'-bifuryl is trans-1,2-dihydroxy-1,2-bis(α, α'-furyl)ethylene, which then rearranges into 2,2'-furoin. The anode-cathode wave of 2,2'-bifuryl has been studied by means of a Kalousek commutator. It has been shown that the polarographic behavior of 2,2'-bifuryl and 2,2'-furoin is similar to that of benzil and benzoin, but differs from the behavior of analogs of the pyridine series.

While the polarographic behavior of benzil and benzoin and also of 2,2'-bipyridyl and 2,2'-pyridoin have been studied by a number of authors [1–12], there has, so far, been no information on the polarographic behavior of 2,2'-bifuryl and 2,2'-furoin. Nevertheless, such information is necessary to answer questions of the analytical determination of these compounds; in particular, the formation of furoin in the oxidation of furfural may be assumed by analogy with the situation in the vapor-phase oxidation of formylpyridine over vanadium catalysts [13]. The polarographic method also permits the study of the kinetics of the oxidation of 2,2'-furoin and the combination of the reductive and protolytic conversions of 2,2'-bifuryl. In this work the mechanism of the electroreduction of 2,2'-bifuryl and 2,2'-furoin at a dropping mercury electrode in aqueous and aqueous-ethanolic solutions at various pH values was studied by classical polarography and by recording curves with a Kalousek commutator.

EXPERIMENTAL

The 2,2'-bifuryl (I) (mp 165°C) and 2,2'-furoin (II) (mp 138–139°C) were purified by two crystallizations from ethanol.

To prepare the initial solutions, weighed samples of I and II were dissolved in water and in ethanol, and then 15-ml portions of the initial solution were mixed with equal volumes of Britton-Robinson buffer solutions having a constant ionic strength $\mu = 0.25$ and pH values from 2 to 12 [14]. The concentration of the depolarizer in the working solutions was from 2×10^{-4} to 1×10^{-3} M.

The working solutions were poured into a thermostated polarographic cell [15] and were deaerated with purified nitrogen previously passed through a bottle containing the polarographic support. The polarograms were recorded at 25.0 ± 0.1°C in the range of potentials from 0 V to the potential of the separation of the support. The anode was a saturated calomel electrode. Accurate values of the potentials were measured separately, after the recording of the polarogram, by means of a high-ohmic direct-current potentiometer but with respect to a second saturated Hg_2Cl_2 electrode. The accuracy of the measurement of the half-wave potentials was ±5–7 mV.

The indicator electrode was a dropping mercury electrode with forced separation of the drop (with a blade) having the following characteristics: $m = 0.81$ mg · sec^{-1}; $t = 0.25$ sec; $m^{2/3} t^{1/6} = 0.69$. The polarograms were recorded on a Tsfassman PE-312 electronic recording polarograph.

The limiting currents (i_l) and half-wave potentials ($E_{1/2}$) of I and II were calculated from the polarograms for various pH values and various concentrations of ethanol in the aqueous ethanolic media, and the slopes of the waves in the semilogarithmic coordinates E versus log $i(i_l - i)$ were determined.

To find the number of electrons n consumed in the electroreduction of one molecule of 2,2'-bifuryl, millicoulometric experiments were carried out by Lingane's method [16]. The number of electrons consumed in the electroreduction of one molecule of 2,2'-furoin was calculated by comparing the height of the wave of this depolarizer with that of the wave of 2,2'-bifuryl.

To study the reversibility of the electroreduction of 2,2'-bifuryl and the characteristics of the unstable intermediate product of its electroreduction—1,2-di(α-furyl)ethane-1,2-diol (III)—polarograms of I were recorded with the use of the Kalousek commutator [17]. The switching of the potential was carried out by means of a transistor circuit with a switching frequency of 11 Hz [18]. The auxiliary potential was kept constant in all experiments (−0.8 V with respect to the saturated calomel electrode).

RESULTS AND DISCUSSION

Electroreduction of 2,2'-bifuryl. In all the solutions studied, the polarograms of 2,2'-bifuryl (I) showed

Half-Wave Potentials, Limiting Currents, and Slopes of the Waves of 2,2'-Bifuryl at Various pH Values on Ordinary Polarograms and Polarograms Taken with a Kalousek Commutator (1×10^{-3} M 50% aqueous-ethanolic solution of the depolarizer in Britton-Robinson buffer solutions); Frequency of the Commutator 11 Hz; $m = 15.36$ mg · sec^{-1}; $t = 1.90$ sec

pH	Integral polarogram			Polarogram with Kalousek commutator							
				wave of I					wave of II		
	$-E_{1/2}$, V	i_l, μA	slope of the wave, mV	$-E_{1/2}$, V	$i_{l,sum}$, μA	i_{cat}, μA	i_{an}, μA	slope of the wave, mV	$-E_{1/2}$, V	i_l, μA	slope of the wave, mV
2.5	0.38	9.42	63	0.34	17.76	4.07	13.69	105	—	—	—
4.1	0.54	9.42	84	0.46	15.00	3.96	11.04	90	—	—	—
5.8	0.59	9.00	94	0.55	14.50	4.07	10.43	136	1.52	1.71	115
6.3	0.65	8.90	84	0.58	13.70	4.07	9.63	163	1.63	2.57	178
9.7	0.79	9.00	94	0.70	12.30	4.07	8.23	131	1.56	2.25	178
10.5	0.71	7.90	94	0.76	7.70	3.21	4.49	116	1.47	2.14	136

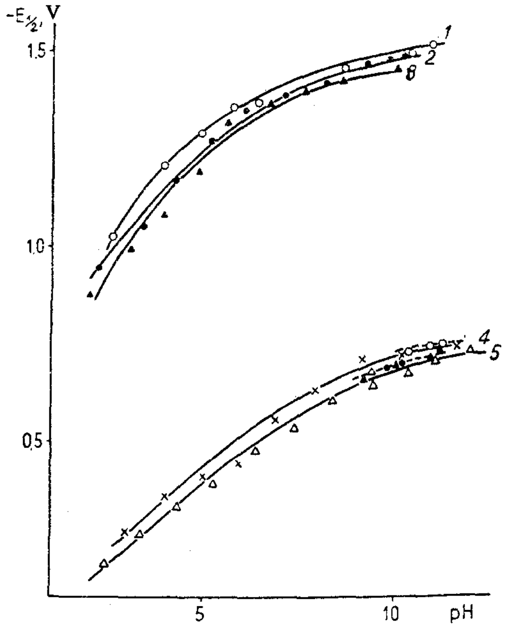


Fig. 1. Half-wave potentials of solutions of bifuryl and furoin (with respect to the saturated calomel electrode) in Britton-Robinson buffer solutions at various pH values: 1) $0.87 \cdot 10^{-3}$ M solution of furoin in 50% ethanol; 2) $0.87 \cdot 10^{-3}$ M solution of furoin in 25% ethanol; 3) $2.5 \cdot 10^{-}$ $\cdot 10^{-4}$ M aqueous solution of furoin; 4) $1 \cdot 10^{-3}$ M solution of bifuryl in 50% ethanol; 5) $1 \cdot 10^{-3}$ M solution of bifuryl in 20% ethanol.

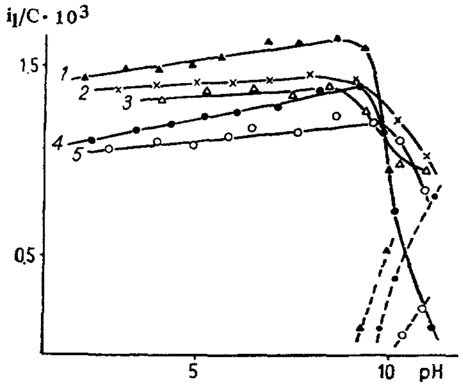


Fig. 2. Limiting current of solutions of bifuryl and furoin in Britton-Robinson buffer solutions on the pH: 1) $2.5 \cdot 10^{-4}$ M aqueous solution of furoin; 2) $1 \cdot 10^{-3}$ M solution of bifuryl in 50% ethanol; 3) $1 \cdot 10^{-3}$ M solution of bifuryl in 20% ethanol; 4) $0.87 \cdot 10^{-3}$ M solution of furoin in 25% ethanol; 5) $0.87 \cdot 10^{-3}$ M solution of furoin in 50% ethanol.

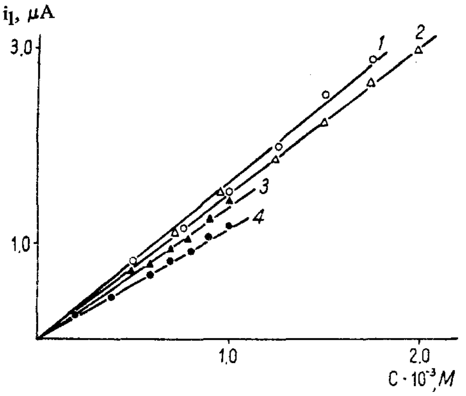


Fig. 3. Calibration curves for the determination of the concentration of 50% ethanolic solutions of bifuryl and furoin from the magnitude of the limiting current: solution of furoin: 1) at pH = 6, 2) at pH = 4; solution of bifuryl: 3) at pH = 4, 4) at pH = 6.

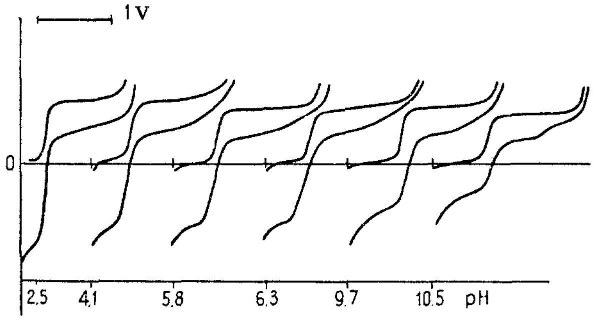


Fig. 4. Polarograms of $1 \cdot 10^{-3}$ M solution of bifuryl in 50% ethanol. All the polarograms, both ordinary ones and those taken with a Kalousek commutator, were recorded from 0 V.

one well-defined electroreduction wave, the $E_{1/2}$ of which varied between −0.2 and −0.7 according to the pH of the medium. In the pH range from 2.0 to 8.0, the $E_{1/2}$ shifted in the direction of more negative potentials by 70 mV/pH unit with a rise in the pH, and then it became almost constant ($\partial E_{1/2}/\partial pH = 16$ mV/pH unit). At pH < 8, the height of the wave of I does not depend on the pH, and then it decreases by 1/3 to 1/2 of its initial value, and at pH 10–11 becomes constant again. The slope of the wave corresponded to 40–58 mV in 20% ethanol and in 50% ethanol at pH > 8.5. Under none of the experimental conditions that we tested was a well-defined second wave located at the potentials of the electroreduction of II observed on the polarograms of I, even when the mercury drop period was increased to 3 sec.

The height of the wave of 2,2'-bifuryl at pH 4 and 6 is proportional to the concentration of the depolarizer in the solution. In this region the wave is a diffusion wave.

In contrast to benzil, in the case of I the presence of borate as a component of the buffer mixture has no appreciable effect on the height of the wave.

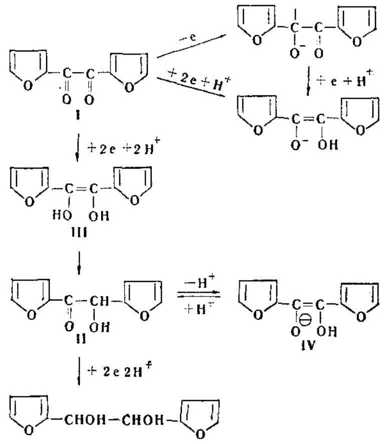
Electroreduction of 2,2'-furoin. The polarograms of 2,2'-furoin (II) in Britton-Robinson buffer solutions containing 0, 10, 15, 25, and 50% of ethanol showed one well-defined electroreduction wave, the $E_{1/2}$ of which varied from −0.95 to −1.50 V according to the pH. In the pH range from 2.0 to 6.5, as the pH is increased $E_{1/2}$ shifts in the direction of more negative potentials by 88 mV/pH unit, and then becomes almost constant ($\partial E_{1/2}/\partial pH = 28$ mV/pH unit) (Fig. 1). The height of the wave scarcely depends on the pH up to pH 9.5 and then falls precipitately in the form of a dissociation curve with pK' = 10.2; together with the fall in the wave a new wave appears and increases in size at more positive potentials corresponding to the potentials of the reduction of 2,2'-bifuryl. It follows from the nature of the dependence of i_l on the height of the mercury column and the temperature that the main reduction wave of II is a diffusion wave. The wave is irreversible: the slope of the wave corresponds to about 80 mV, reaching 120–150 mV in individual cases. In the pH range from 4 to 5, a diffuse doubling of the wave takes place, the sum of the two parts of the wave remaining constant.

The height of the wave of 2,2'-furoin in acid media at pH 3, 4, and 6 is proportional to the concentration of 2,2'-furoin in the solution.

Millicoulometric experiments showed that the electrochemical process responsible for the appearance of the polarographic wave of I is a two-electron process ($n \approx 1.8$). It follows from the approximately identical heights of the waves in the polarograms of I and II that the electroreduction of II is also a two-electron process.

In the case of 2,2'-bifuryl, the polarograms recorded with the Kalousek commutator technique showed a fused (irreversible) anode-cathode wave, the $E_{1/2}$ and i_l values of which are shown in the table. In addition, in this case a new cathode wave located at the potentials of the electroreduction of II also appeared on the polarogram; the height of this wave rose with an increase in the pH simultaneously with a fall in the height of the anodic part of the mixed cathode-anode wave.

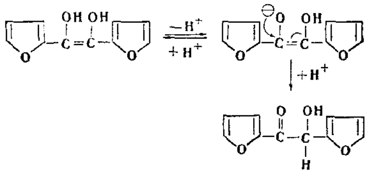
The experimental results obtained permit us to assume the following association of processes leading to the appearance of the polarographic waves of I and II.



The electroreduction of II takes place as a typical electroreduction of a heteroaromatic ketone, like the electroreduction of 2-acetylfuran, and at approximately the same values of the electrode potentials [19]. The indistinct splitting of the wave found at pH 4–5 corresponds to the competing electroreduction of the protonated and the unprotonated carbonyl groups [20]. The decrease in the wave of II in alkaline media at pH > 9.5 is a consequence of two processes: the conversion of the 2,2'-furoin into the form of the mesomeric anion IV (cf. [12]) and the chemical oxidation of the anion IV to bifuryl, which is observed simultaneously at the same pH values.

Because of the presence of an α-dicarbonyl grouping in the molecule, the electroreduction of I takes place at considerably more positive potentials (by 700–800 mV) than the electroreduction of II. It would appear that the two-electron reduction of I could lead to the formation of II, which would then give its characteristic wave on the polarogram. However, the direct electroreduction of I leads not to II but to an intermediate product III (or, in alkaline media, to the radical-anion IV, in consequence of which the height of the wave decreases).

The isomerization of III into II takes place under the action of OH^- ions as an acid-base reaction through the formation of an ambident anion:



The rate of isomerization consequently depends on the protolysis constant of the enediol (III): the lower this is the higher is the pH required for the creation of the necessary concentration of the anion. In this way it is possible to explain why the second wave is observed on the Kalousek polarograms only at fairly high pH values and is not found in an acid medium at all. It may appear incomprehensible why the second wave, corresponding to the formation of II from I, appears only on the Kalousek polarograms and not on conventional polarograms: if the isomerization of II into III requires a certain time and cannot take place on a mercury drop even with a life of 3 sec, how can it take place at a commutator in a shorter time? The explanation apparently consists in the fact that at the potentials of the electroreduction of II (from –1.4 to –1.5 V) there is already a considerable desorption of the molecules of the depolarizer; using the Kalousek commutator we systematically return the potential from –0.8 to –1.2 V, where the primary product of the electroreduction of III is absorbed and where it possesses a high reactivity.

It follows from a comparison with literature data [9] that the enediol III has the trans configuration, since only the trans-enediol gives a fused cathode-anode wave with an α-diketone.

The polarographic behavior of 2, 2'-bifuryl and 2, 2'-furoin is similar to that of benzil and benzoin, but, in the case of the compounds of the furan series, the conversion of the enediol into furoin takes place more slowly than the isomerization of stilbenediol into benzoin. At the same time, the behavior of these compounds differs fairly sharply from the behavior of the corresponding derivatives of the pyridine series [11, 12].

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