INVESTIGATIONS IN THE FIELD OF AROMATIC HETEROCYCLES

VIII. Polarographic Reduction of Piazthiole and Piazselenole in Aqueous Solutions*

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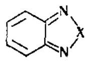
Piazthiole and piazselenole, like benzofurazan, studied previously, are reduced at the dropping mercury electrode with the consumption of six electrons and with the formation of o-phenylenediamine. The transfer of the first electron in acid solutions is preceded by the reversible protonation of the molecules. The ease of reduction rises in the sequence benzofurazan, piazthiole, piazselenole in accordance with a fall, and not with a rise, in the electronegativity of the key heteroatoms O, S, Se and with the decrease in the dipole moments of the corresponding molecules. The presence of two waves in the polarogram of piazselenole is due not to the stagewise nature of its reduction but to the anodic dissolution of mercury in the presence of hydrogen selenide.

The structure of benzofurazan (I), piazthiole (II), and piazselenole (III) is not completely clear at the present time. These compounds belong to the class of 1, 2, 5-X-diazoles and, as can be seen from the formula, differ only in the key heteroatom X.



I X = O, II X = S, III X = Se

It has been calculated (see, for example, [2]), that the conversion of benzene derivatives into systems I–III is associated with a disturbance of the equivalence of the bonds, the degree of which rises with an increase in the electronegativity of the key heteroatom. It was concluded that such a disturbance of the equivalence of the bonds ends with the formation of an o-quinoid ring as a structural element of the corresponding plane molecules [3, 4]. At the same time, a naphthalene-like structure has been assumed for compounds II–III [5] and the existence of structures with tetravalent X-atoms (X = S, Se) has ever been suggested [6, 7]. The necessity for a further critical discussion of the question of the close similarity of these compounds with naphthalene is also reflected in the literature [8].

In preceding communications of this series the point of view has been developed according to which the formation of compounds I–III is accompanied by the appearance of new aromatic systems which differ from naphthalene and from one another in the effective participation of the key heteroatom in the formation of an annular cloud of delocalized electrons. In order to compare this capacity for conjugation of O, S, and Se atoms with their electronegativities, we turned to the electrochemical reduction of compounds I–III. In this, we hoped that their tendency to reduction, expressed through the half-wave potentials, would depend on the electronegativity of the only varying portion of the molecule—the atom X. As Voitkevich [9] has shown, the ease of reduction increases with an increase in the dipole moment. According to Hill and Sutton [10], the passage from S to Se and to O leads to a sharp rise in the dipole moment in the sequence of compounds I–III (μ = 4.03, 1.73, and 0.94 D, respectively). It was, therefore, to be expected that the ease of reduction should increase in the same sequence. It follows from chemical data that compounds I–III are reduced with the opening of the ring and with the formation of o-phenylenediamine [11]. In this process, in accordance with the formulas of I–III, six electrons must be consumed. Eight electrons should be consumed for the reduction of structures with quatervalent X-atoms. A number of electrons consumed averaging between 6 and 8 would indicate an "averaged" valence state of the S-atom in piazthiole and of the Se atom in piazselenole.

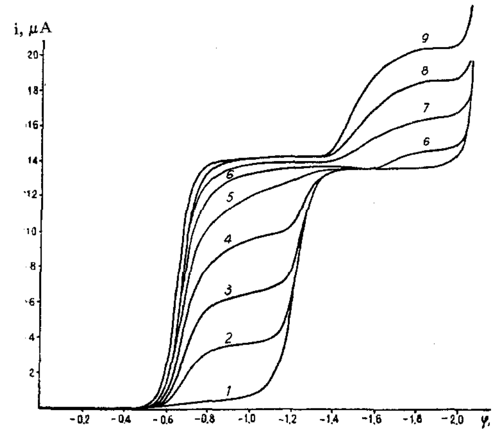


Fig. 1. Influence of acidification on the polarogram of piazthiole in 0.1 M $LiClO_4$ containing 0.02% of gelatin. Concentration of piazthiole: 10^{-3} M. Concentration of HCl: 1) 0; 2) $4.5 \cdot 10^{-4}$; 3) $8.6 \cdot 10^{-4}$; 4) $1.24 \cdot 10^{-3}$; 5) $1.58 \cdot 10^{-3}$; 6) $1.9 \cdot 10^{-3}$; 7) $2.2 \cdot 10^{-3}$; 8) $2.48 \cdot 10^{-3}$; 9) $2.74 \cdot 10^{-3}$ M. The HCl solution also contained 10^{-3} M of piazthiole so that when the acid was added the concentration of piazthiole remained strictly constant. For clarity, the oscillations have been smoothed out.

Benzofurazan (I) can be obtained by the dehydration of o-benzoquinone dioxime [12]. The formation of piazselenole (III) takes place readily when o-phenylenediamine is oxidized with selenium dioxide [13]. It has been shown [11] that the oxidation takes place

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*For part VII, see [1].

through the stage of o-quinone diimine or a derivative of it capable of adding HCl. On the other hand, it is known that 2-aminothionylaniline can be converted into piazthiole [14]. On the basis of the data given on the methods of preparation it is, of course, impossible to judge the features of the structure of the compounds obtained, but it is possible to raise the question of the nature of the particles formed as intermediates in the electrochemical reduction of compounds **I–III.** It was of interest to determine whether this process involves the stepwise cleavage of the ring, whether the intermediate particles retain the heteroatom in the side chain, or whether cleavage takes place with the formation of o-benzoquinone diimine. In the latter case, it must be borne in mind that the fixation of the stage of the formation of o-benzoquinone diimine is unlikely, since imino derivatives of carbonyl compounds are reduced more readily than the carbonyl compounds themselves, and the wave of o-benzoquinone at pH = 5 has $\varphi_{1/2}$ = = +0.25 V [15]. In the case of piazselenole (III), the appearance of the anode wave of another reduction product—hydrogen selenide—may also be expected [16]:

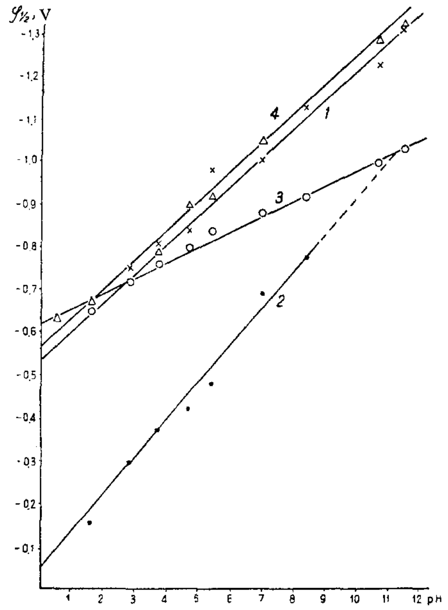


Fig. 2. Influence of the pH on the half-wave potential of piazthiole (1), on the first (2), and second (3) waves of piazselenole, and of benzofurazan (4).

$$\mathrm{Hg} + \mathrm{H_2Se} \rightarrow \mathrm{HgSe} + 2\mathrm{H}^+ + 2e^-$$

This process may manifest itself since **III**, according to preliminary results [11], is reduced at moderately negative potentials. The existence of process (1) in the general scheme of conversions imparts an apparently two-stage nature to the reduction of piazselenole. In principle, this phenomenon is also possible for piazthiole **II.**

Apart from the preliminary figures mentioned [11], which were obtained in acetate buffer solution, there are no data on the polarographic reduction of compounds II and III in aqueous solutions (le Pērnte's paper [7] is purely analytical).

The polarographic behavior of benzofurazan has been studied in detail against a background of a universal buffer (Britton-Robinson)—aqueous-ethanolic solution containing 30% of ethanol (by volume). Under these conditions one six-electron wave was found, which corresponds to reduction with the opening of the heterocycle and the direct formation of o-phenylenediamine [17]. In the present paper we give the results of a study of the polarographic behavior of piazthiole and piazselenole in unbuffered and buffered aqueous solutions. In order to compare $\varphi_{1/2}$ of all three compounds obtained under strictly identical conditions, $\varphi_{1/2}$ for benzofurazan was determined again in the buffer solutions used for II and III.

EXPERIMENTAL

The polarograms were recorded with a Hungarian OH-102 electronic polarograph. Coupled with the dropping mercury electrode, a saturated calomel electrode was used.

The number of electrons was found microcoulometrically [18]. With the object of accumulating and identifying the reduction products of piazthiole and piazselenole, the electrolysis of 5 ml of solution was carried out at a stationary mercury cathode with an area of about 0.5 cm^2. This experiment was carried out with a Czechoslovakian LP-60 electronic polarograph, with which considerable currents (up to 5 mA) can be measured. The electrolysis products were subjected to polarographic and chemical qualitative analysis.

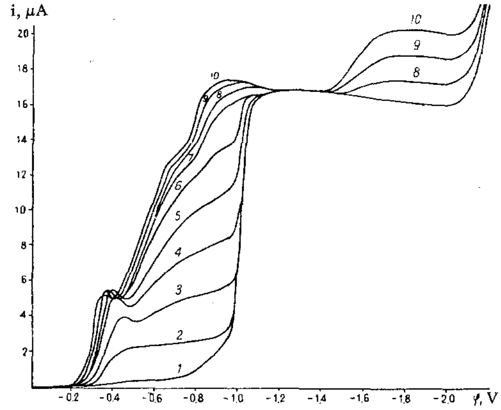


Fig. 3. Influence of acidification on the polarogram of piazselenole (10^{-3}M) in 0.1 M $LiClO_4$ solution containing 0.02% of gelatin. Concentration of HCl: 1) 0; 2) 4.5 · 10^{-4}; 3) 8.6 · 10^{-4}; 4) 1.24 · 10^{-3}; 5) 1.58 · 10^{-3}; 6) 1.9 · 10^{-3}; 7) 2.2 · 10^{-3}; 8) 2.40 · 10^{-3}; 9) 2.74 · 10^{-3}; 10) 2.98 · 10^{-3} M. The solution of HCl contained 10^{-3} M piazselenole so that the concentration of piazselenole in the cell remained strictly constant. For clarity, the curves have been plotted with leveling out of the oscillations.

The piazthiole and piazselenole were synthesized by Hinsberg's method [13]. Lithium perchlorate was used as the inert electrolyte in the unbuffered solutions. The components of the buffer mixtures—according to Walpole (sodium acetate and hydrochloric acid) for pH = 0.65–5.2 and according to Britton and Welford (monopotassium phosphate and sodium hydroxide) for pH = 5.8–12—were additionally purified by recrystallization. The hydrochloric acid solutions were prepared from Fixanal products. Only double-distilled water was used to prepare the solutions. The oxygen was displaced from the solutions with argon.

Piazthiole is appreciably volatile. When the dissolved air was displaced by argon, part of the piazthiole was lost. To find the true value of the limiting current, polarograms were recorded after various intervals of time with the passage of argon through the solution between measurements. The dependence of the height of the wave on the time of passage of argon was extrapolated to zero time. In some experiments the time of passage of argon was reduced to the necessary minimum. Benzofurazan is even more volatile. Piazselenole is nonvolatile.

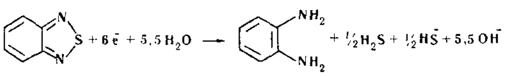
Piazthiole (II). In the polarogram of piazthiole in an unbuffered medium, namely on a support of 0.1 M aqueous $LiClO_4$, there are two waves. The first wave is an adsorption prewave. If the solution contains gelatin to suppress the maxima, this wave does not appear.

The half-wave potential of the second, main wave, is −1.22 V. Its limiting current is proportional to the concentration of piazthiole and is determined by the rate of its diffusion.

It was established by microcoulometric measurements that six electrons take part in the reduction of one molecule of piazthiole. On the polarogram of partially reduced piazthiole, in addition to the wave of the reduction of the remainder of the piazthiole, there is an anode wave which, from all indications, corresponds to the anodic dissolution of the mercury in the presence of the accumulated sulfide ion with the formation of mercury sulfide. In an acidified solution the smell of hydrogen sulfide can be distinctly detected. The qualitative reaction for the S^{2-} ion is positive.

Hydrogen ions must be consumed in the reduction of piazthiole. To investigate the stoichiometry of the reaction with respect to hydrogen ions, an experiment was carried out with the acidification of an unbuffered solution of piazthiole (Fig. 1). On the polarogram of a weakly acidic solution of piazthiole a new wave arises approximately 0.5 V more positive than the piazthiole wave in a neutral medium. When the concentration of acid is increased, the new wave rises at the expense of the main wave. The combined limiting currents of the two waves do not change until the new wave takes over the main wave completely. Further acidification leads to the appearance of yet another wave with a half-wave potential of −1.5 V, which corresponds to the discharge of the superfluous hydrogen ions; the piazthiole wave with a half-wave potential of about −0.7 V no longer appears.

By means of the theory of latent limiting currents [19, 20], the number of protons (q) participating in the reduction of piazthiole was found to be 5.5. The reduction of piazthiole in an unbuffered neutral medium can be expressed by the equation:



(2)

The reaction products are o-phenylenediamine and an equimolar mixture of H_2S and HS^-.

In a buffer solution, piazthiole gives a single diffusion wave over the whole pH range. The half-wave potential becomes more negative by 70 mV with a rise in the pH of 1 unit (Fig. 2, curve 1). An analysis of the shape of the piazthiole wave in a buffer solution showed that the coefficient 2.3RT/αnF from the wave equation is 50 mV and the transfer coefficient $\alpha = 0.2$. Consequently, the reduction of piazthiole is a completely irreversible process. Therefore the appearance of a new wave in unbuffered acid media and the dependence of the half-wave potential on the pH in buffer solutions are due to preliminary protonation.

Using the Ilkovič equation, the diffusion coefficient of piazthiole was calculated from the limiting current in 0.1 M $LiClO_4$. It is $5 \cdot 10^{-6}$ cm²/sec.

Piazselenole (III). In the polarography of piazselenole there is much in common with that of piazthiole, which is due to the similarity of the structures and the chemical properties of these two compounds. There is also, however, a fundamental difference which is due to the simultaneous occurrence of the anodic dissolution of the mercury in the presence of the selenide ion arising in the reduction of the piazselenole.

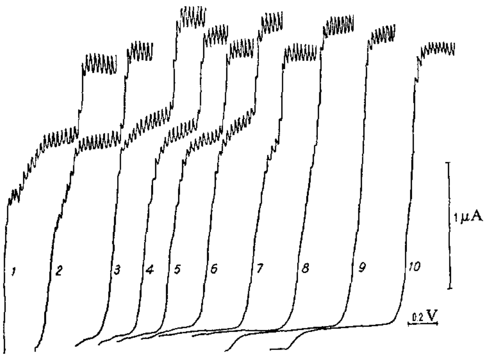
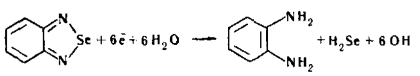


Fig. 4. Polarograms of piazselenole ($2 \cdot 10^{-4}$ M) in buffer solutions. pH: 1) 0.5; 2) 1.6; 3) 2.8; 4) 3.7; 5) 4.7; 6) 5.2; 7) 7.0; 8) 8.4; 9) 10.4; 10) 11.5.

As in the case of piazthiole, in neutral unbuffered solution piazselenole forms two waves with half-wave potentials of about −0.75 and −1.05 V, the first of which is an adsorption wave and the second a diffusion wave. The diffusion coefficient of piazselenole was found from the Ilkovič equation to be $5.3 \cdot 10^{-6}$ cm²/sec.

From the results of microcoulometric measurements for piazselenole, again $n = 6$. On a polarogram of a partially reduced solution of piazselenole the anode wave of the selenide ion appears. If air is admitted to the cell, the mercury on the bottom is rapidly covered with a red deposit of elementary selenium and the anode wave disappears.

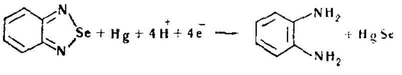
As in the case of piazthiole, when an unbuffered solution of piazselenole is acidified a new wave appears on the polarogram (Fig. 3). With an increase in the concentration of the acid it rises at the expense of the main wave; after reaching the height of the main wave its rise ceases and the wave of the discharge of the excess hydrogen ions appears. As can be seen from Fig. 3, in acid solutions a new adsorption wave again appears which is higher than the adsorption preliminary wave in neutral solution. Moreover, the new diffusion wave is split (curves 6–10). These phenomena are connected with the anodic dissolution of mercury in the presence of selenide ions. The number of protons q participating in the reduction of the piazselenole was found to be 6. This corresponds to the occurrence of the over-all reaction (in a neutral medium):



(3)

In buffer solutions at pH > 9, there is only one diffusion wave on the polarogram of piazselenole; in the range pH ≈ 3–8 there are two diffusion waves and at pH < 3 there are three waves of which the first is an adsorption wave (Fig. 4). The half-wave potentials of the diffusion waves depend on the pH, the dependence being more pronounced for the first wave ($\partial\varphi_{1/2}/\partial pH = 87$ mV) (see Fig. 2, curve 2) than for the second wave ($\partial\varphi_{1/2}/\partial pH = 36$ mV) (Fig. 2, curve 3).

In considering the data presented, we adopt the following mechanism of the electrode processes. Let the reduction of piazselenole take place according to reaction (3) over the whole range of potentials, i.e., with the transfer of six electrons in a single stage. At the potentials of the first wave with pH < 8, the anode reaction (1) may take place simultaneously with reaction (3) and the over-all process must be represented by the equation:



(4)

Then, with a shift of the potential in the negative direction a value of it will be reached at which reaction (1) ceases and, because of this, a second step appears on the polarogram. The total limiting current will correspond to the transfer of six electrons and not to four as before. Thus, the presence of two waves on the polarogram of piazselenole need not be connected with a stage mechanism of its reduction.

The experimental data agree with these ideas. The dependence of $\varphi_{1/2}$ of the first wave on the pH reflects the protonation preceding the slow transfer of the first electron from the electrode to the protonated molecule.

The magnitude $\partial\varphi_{1/2}/\partial pH$ for the second wave (36 mV) closely corresponds to that which should exist for reaction (1). The equation of the wave for reaction (1) has the form:

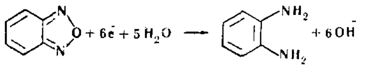
$$\varphi=\varphi^\circ_{Hg^{2+}}-\frac{2.3RT}{2F}\lg\frac{i_d-i}{\varkappa}-\frac{-2.3RT}{2F}pH$$

$$\text{and}\ \partial\varphi/\partial pH=\frac{2.3RT}{2F}\approx 29\ \text{mV}. \qquad (5)$$

Reaction (1) must be fast and even reversible. This was confirmed by special experiments with alternating-current polarography.

Benzofurazan (I). Measurements of polarograms of benzofurazan over a wider pH range than in the preceding work [17] showed that $\varphi_{1/2}$ depends on the pH over the whole range of pH values (Fig. 2, curve 4). The straight lines $\varphi_{1/2} = f(pH)$ for benzofurazan and piazthiole are parallel. The differences in the values of $\varphi_{1/2}$ for benzofurazan in the previous work [17] and those in this paper are obviously due to the fact that the measurements were carried out in different buffer solutions.

When an unbuffered solution of benzofurazan was acidified, as in the two previous cases a new wave appeared, corresponding to the reduction of previously protonated benzofurazan. When benzofurazan was added to a solution of acid, the total limiting current did not change. Consequently, q = n and the reaction in a neutral unbuffered medium takes place in accordance with the equation:



(6)

The diffusion coefficient of benzofurazan calculated from its limiting current by means of the Ilkovič equation is $6\cdot10^{-6}$ cm^2/sec.

DISCUSSION OF THE RESULTS

It follows from what has been said that benzofurazan, piazthiole, and piazselenole undergo reduction in an identical manner in aqueous solutions: six electrons are consumed per molecule and o-phenylenediamine is formed. The consumption of six electrons in the reduction of piazthiole or piazselenole means that the X-atoms in the molecules of the compounds taking up the electrons are present in fact in the bivalent state. The two-wave polarogram of piazselenole in acid media does not reflect the stagewise nature of the process, only the peculiar behavior of the second reduction product—hydrogen selenide. The absence of stages in the reduction of piazthiole is due to the fact that the anode process with the sulfide ion from the piazthiole takes place in a potential range that has not been investigated. The slow stage in the reduction of compounds I–III is the transfer of the first electron, and all the subsequent conversions take place rapidly. As was assumed, the complete splitting off of the heteroatom takes place and the process does not stop at the stage of the formation of o-quinone diimine.

Another feature of the polarographic behavior of compounds I–III is that the transfer of the first electron is preceded by reversible protonation. The dependence of $\varphi_{1/2}$ on the pH in buffer media which this explains is observed over the whole pH range studied from 0 to 12. Since compounds I–III exist in the form of salts only in strongly acid solutions, the recombination of I–III with proton donors under polarographic conditions must take place at high rates. It is possible that protonation is facilitated by the reduction of compounds I–III not only because of the appearance of an effective positive charge on them but also because of a definite change in the electronic structure of the molecule.

Identical reduction mechanisms are a condition the fulfillment of which is a necessary requirement for a comparison of the values of $\varphi_{1/2}$ in elucidating the connection between the structure of the molecules and their reactivities. Since in this case the reduction mechanisms are identical, $\varphi_{1/2}$ can be used for a qualitative comparison of the electron affinities of the molecules I–III. Since, however, the process is irreversible and $\varphi_{1/2}$ is a function of the pH, a simple comparison of $\varphi_{1/2}$ cannot give a quantitative picture of the reactivities of the molecules I–III. The influence of the structure of the electric double layer on $\varphi_{1/2}$ of the irreversible wave introduces an indeterminacy, since it is different at different values of $\varphi_{1/2}$. In the second place, where $\varphi_{1/2}$ depends on the pH, $\varphi_{1/2}$ is compared at a single pH value. Since the acid-base properties of compounds I–III cannot be the same, this method of comparing $\varphi_{1/2}$ is not unobjectionable. These two circumstances make the influence of fine structural effects problematical but, apparently, cannot affect the quantitative evaluation of more considerable differences. A comparison of the reactivities of compounds I–III is included among such simpler problems.

As follows from Fig. 2, benzofurazan is reduced with the greatest difficulty. Piazthiole occupies an intermediate position, and piazselenole is reduced most easily. For the latter the value of $\varphi_{1/2}$ for the first wave must be taken. Thus, at pH = 7, the values of $\varphi_{1/2}$ for I–III are, respectively, –1.05, –1.00, and –0.65 V. Contrary to what was expected, the ease of reduction rises in the sequence benzofurazan, piazthiole, piazselenole in accordance with a rise, and not with a fall, in the electronegativity of the key heteroatoms O, S, and Se and with a decrease in the dipole moments of these molecules. This conclusion also follows from the position of the line 1 between the lines 4 and 2 drawn through the system of experimental points in Fig. 2. At pH values from 3 to 4 the concrete values of $\varphi_{1/2}$ fall in the sequence III, I, II. The difference between the values of $\varphi_{1/2}$ for benzofurazan and piazthiole is anomalously small in comparison with the difference between the values of $\varphi_{1/2}$ for piazthiole and piazselenole. Nevertheless, the electronegativity of the key heteroatom changes far more strongly on passing from oxygen to sulfur than in the subsequent passage from sulfur to selenium.

Whether these anomalies reflect deeper structural differences in compounds **I–III** or are connected with the above-mentioned difficulties in comparing $\varphi_{1/2}$ cannot yet be decided. The polarography of compounds of the 1, 2, 5-X-diazole series in an aprotic medium will perhaps throw additional light on this problem.

The waves of benzofurazan, piazthiole, and piazselenole are convenient for analytical use. Thanks to the presence of a rapid stage of the anodic dissolution of mercury in the presence of hydrogen selenide, piazselenole can be determined in very low concentrations by alternating-current polarography.

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