ELECTROREDUCTION OF BENZO-1,2,3-DITHIAZOLIUM SALTS AND THEIR SELENIUM ANALOGS IN NONAQUEOUS SOLUTION

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The electroreduction of benzo-1,2,3-dithiazolium cations and their selenium analogs in aprotic solvents takes place in two steps. The first step is a reversible, one-electron transfer leading to the formation of stable radicals detected by EPR. As a result of further electroreduction, the radicals obtained combine with six electrons to form the corresponding o-aminothio(seleno)phenols. Analysis of the reduction potentials of the compounds studied shows that the substitution of a selenium atom for a sulfur in these cations, especially in the 2 position of the heterocycle, facilitates their electrochemical reduction. The electrochemical activity and the kinetics of nulceophilic substitution in the cations studied are compared.

Benzo-1,2,3-dithiazolium cations (I) and their selenium analogs (II)-(IV) are convenient models for studying the effect of the nature and arrangement of the heteroatoms on the acceptor properties of the heterocycle. Our data [1-7] show these factors to have a substantial effect on the reactivity and spectral properties of the cations.

An investigation of the electrochemical reduction of (I)-(IV) perchlorates in protic solvents [8, 9] showed that the basic factors influencing the polarographic behavior of the salts are the stability of the initial depolarizers and the adsorbability of their reduction products on the electrodes. All of the enumerated cations irreversibly add seven electrons in one step, which leads to the opening of the rings and the splitting out of the heteroatom in the 2 position in the form of sulfide or selenide ion. The presence of S^{2-} or Se^{2-} in the preelectrode layer in protic solvents causes a shift in the redox potential of the mercury drop electrode because of the formation of insoluble mercury salts.

The size of this shift depends on the nature of the heteroatom in the 2 position which forms the anion of the mercury salt, on the region of the reduction potential of the initial depolarizer, and on the acidity of the solution. This markedly complicates the polarogram of the cations. It was concluded from the results of a study of the electrode process with the parallel occurrence of the electroreduction of the (I)-(IV) cations and the anodic dissolution of mercury in the presence of sulfide and selenide ions that the polarographic behavior of the cations studied in protic solvents did not afford a comparison of their acceptor properties. In our opinion, the complexity of the polarograms in proton-donating solvents is also related to the possible protonation of intermediate reduction products to form depolarizers which are stronger oxidants than the initial compounds.

In order to eliminate the possibility of adsorption and protonation of the reduction products and to preclude their hydrolysis or solvolysis, we have studied the polarographic behavior of the (I)-(IV) salts in acetonitrile with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. All of the cations give polarograms with the same number of waves of similar morphology in this system. The reduction takes place stepwise under these conditions. Two waves are found on the polarograms with the second almost six times higher than the first.

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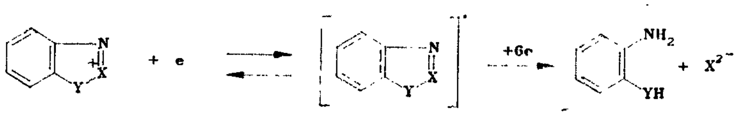
On analyzing the parameters of these polarograms, we come to the conclusion that the difference in the character of the electrochemical behavior of the (I)-(IV) salts arises solely as a consequence of the difference in their first half-wave potentials. The limiting currents of both waves are diffusion limited for all of the cations studied, and the $E_{1/2}$ values do not depend on the depolarizer concentration. In preparative electrolysis with a stationary mercury electrode in the region of the potentials of the first waves of the (I)-(IV) salts, the color of the solutions deepens. The depth and intensity of this color is maintained for several minutes, even when the voltage to the electrolyzer electrodes is switched off. They depend on the nature of the cation and the duration of the electrolysis. On polarograms taken in the reduced solutions, an anodic—cathodic wave arises which preserves the height of the limiting diffusion current of the second wave. Admission of air to the cell causes the rapid disappearance of the color and the restoration of the initial polarogram.

Application of the equation for a reversible wave to the shape of the first waves of the (I)-(IV) salts shows that they are reversible. Cyclic voltammetry affords further evidence of this. The cyclic voltammograms obtained with a rotating, amalgamated silver electrode have a cathodic and anodic peak, the shift between which is 0.055-0.070 V, in the region of the potentials of the limiting current of the first waves of the cations on classical voltammograms.

In view of the above, and also of results obtained earlier in the reduction of derivatives of N-(alkylthio)- and N-(alkylseleno)diazoles [10, 11] with structures similar to that of the (I)-(IV) cations, it can be hypothesized that the first step in the electroreduction of the salts studied is a one-electron transfer leading to the formation of the corresponding, stable, free radicals:



I-IV

I X=Y=S; II X=Y=Se; III X=S, Y=Se; IV X=Se, Y=S

Direct indication of their formation under the conditions of electrochemical reduction is given by the EPR spectra recorded at the potentials of the first waves of the (I)-(IV) cations in a microelectrolyzer placed directly in the cavity of the EPR spectrometer. The nature of the spectra and the values of the hyperfine structure constants of the free radicals do not depend on the nature of atom X (X = S, Se) in the heteroring, within the limits of resolution of the spectrometer. As an example, Fig. 1 shows the EPR spectrum of the radical obtained from the (I) cation. In the spectrum there is a singlet with well-resolved structure which confirms the structure of the (I) radical. The hyperfine constants are: $a_N = 8.82$, $a_{4-H} = 2.85$, $a_{6-H} = 0.42$, and $a_{7-H} = 0.84$ Oe.

The second, irreversible, six-electron-wave reduction of the (I)-(IV) salts is located in the extremely negative region and corresponds to the further reduction of the free radicals being formed in the first step. The reduction products in the second wave are the corresponding sulfide or selenide ion and aminothio- or aminoselenophenol.

The reduction products were determined qualitatively in the bulk solutions of the (I)-(IV) salts after microelectrolysis. The first, $E^A_{1/2}$, and second, $E^B_{1/2}$, half-wave potentials obtained by the reduction of the cations studied are shown in Table 1.

All of the cations studied are conveniently characterized by a simple mechanism of the electrode reaction consisting of a reversible electron transfer at the first step, which is uncomplicated by adsorption and subsequent chemical reaction. Thus, an analysis of the first step of the polarographic reduction allows one to evaluate the connection between the nature and arrangement of the heteroatoms in the (I)-(IV) cations and their fine structure and reactivity.

Comparing the $E_{1/2}$ potentials of the first wave of these salts (Table 1), we are led to the conclusion that in comparison with the benzo-2,1,3-thiadiazolium and benzo-2,1,3-selenadiazolium cations we studied previously [12, 13], reduction is considerably facilitated by the

TABLE 1. Half-Wave Reduction Potentials of the (I)-(IV) Salts (in acetonitrile)

Cation	$-E^{A}_{1/2}$, V	$-E^{B}_{1/2}$, V
I	0,26	2,22
II	0,15	2,11
III	0,25	2,20
IV	0,15	2,10

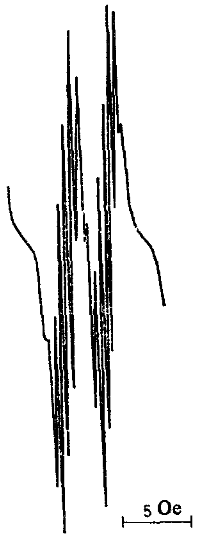


Fig. 1. The EPR spectrum of the benzo-1,2,3-dithiazolium perchlorate radical in 0.1 N $(C_2H_5)_4NClO_4$ in acetonitrile.

introduction of a second, sulfur or selenium, heteroatom into the heterocycle, whereas the half-wave potential is substantially influenced only by the nature of the heteroatom in the 2 position. The selenium-containing cations are more easily reduced than their sulfur analogs. As can be seen from Table 1, the replacement of a sulfur atom in the 2 position by a selenium atom (cations (I) and (III)) shifts the value of $E_1/_2$ by more than 0.1 V in the positive direction.

The change in reactivity towards electroreduction in the (I)-(IV) series is not due to the electronegativities of the heteroatoms, the values of which for sulfur and selenium are close together (2.55 and 2.58, respectively [14]). The greater ease of reduction of the (I)-(IV) cations compared to the benzo-2,1,3-thia(selena)diazole cations (V, VI) [12, 13] also testifies to this point. The replacement of a nitrogen atom (electronegativity 3.04) by an atom of sulfur or selenium, with electronegativity of 2.58 or 2.55, markedly increases the oxidation potential of the cation.

Thus, the cations studied can be arranged in the following series in order of ease of electroreduction: (V) < (I) < (III) < (IV) < (II). It should be noted that the differences in reduction potentials of the (I)-(V) salts do not show up on the general picture of their polarographic behavior, which is evidence of the similarity of the reaction mechanisms.

Quantum-chemical calculation of cation (I) [7] showed that the characteristic feature of the compounds studied is the delocalization of the positive charge of the heteroring with its transfer to the condensed benzene nucleus. Replacement of a sulfur atom by a selenium atom, especially in the 2 position, leads to a substantial increase in the contribution of structures with transfer of charge on going from salt (I) to its selenium analogs (II)-(IV).

It is characteristic that the activity series of the (I)-(IV) cations towards nucleophilic substitution reactions with aromatic amines [6, 7] coincides with their ease of polarographic reduction.

EXPERIMENTAL

The perchlorates of compounds (I)-(IV) were obtained by the methods described in [1-3, 7]. Chromatographically pure samples were used for the polarographic measurements and the experiments involving EPR. The acetonitrile was purified by the method in [15]. We used a capillary with the following characteristics: $m = 1.1$ mg/sec; $t = 3.5$ sec in 0.1 N aqueous KCl with a mercury column 50 cm high and an open circuit. The second electrode was mercury in contact with a solution of the supporting electrolyte, tetraethylammonium perchlorate, and separated from the solution being studied by a fritted glass filter. The electrode potentials were measured with respect to an aqueous, saturated calomel electrode with no correction for the interphase potential. We recorded the polarograms and carried out the preparative electrolyses at a stationary mercury electrode (a mercury pool of about 0.8 cm^2 area) in a single cell of Jena instrument glass.

Polarograms were recorded on an LP-60 polarograph. Cyclic voltammograms were taken on a PO-5122 (model 03) oscillographic polarograph. EPR spectra were recorded on a Rubin spectrometer at room temperature.

Oxygen was purged from the solutions studied with a stream of purified argon.

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