Electroreduction mechanism of *N*-phenylhydroxylamines in aprotic solvents: formation of hydrogen bonds between *N*-(3-nitrophenyl)hydroxylamine and its radical anion

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The electroreduction of *N*-(3-nitrophenyl)hydroxylamine in DMF was studied using cyclic voltammetry, chronoamperometry, and numerical simulation. It is shown that the stability of formed radical anion is significantly higher than that of the radical anion of the 4-nitrophenyl derivative. In the range of low concentrations and high potential scan rates, the electroreduction of *N*-(3-nitrophenyl)hydroxylamine is complicated only by the formation of complexes between the depolarizer molecules, most likely, due to hydrogen bonds, as well as between the depolarizer and its radical anion. The thermodynamic and kinetic parameters of these processes were evaluated.

Key words: *N*-arylhydroxylamines, radical anions, hydrogen bond, cyclic voltammetry, chronoamperometry, numerical simulation.

The reduction of the hydroxylamino group is the final reaction of the multistep process of practically significant electrochemical reduction (ER) of nitro compounds to the corresponding amines.[1] Our study of the ER of *N*-(4-nitrophenyl)hydroxylamine (**1**) in aprotic solvents performed using experimental and theoretical methods shows that the radical anion (RA) of this compound formed upon the electron transfer

$$\text{ArNHOH} \xrightarrow[E^\circ_1]{\text{e}^-} \text{ArNHOH}^{\cdot-} \qquad (1)$$
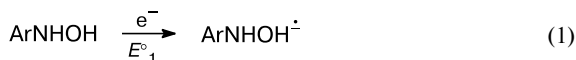
is unstable and undergoes the fast cleavage of the N—OH bond with hydroxide anion elimination.[2]

As shown by the results of quantum chemical calculations,[3,4] the high rate of this reaction is caused by the fact that the singly occupied molecular orbital of the RA of compound **1** has a nodal plane passing through the N—OH bond. As a consequence, the presence of an electron on this orbital results in the destabilization of this bond. At the same time, according to the calculations, there is no density of unpaired electron on the hydroxylamino group in the RA of *N*-(3-nitrophenyl)-hydroxylamine (**2**). The latter suggests that the RA of compound **2** should by much more stable than the RA of compound **1**. To check this conclusion, we studied the ER process of compound **2** by electroanalytical methods.

1   **2**
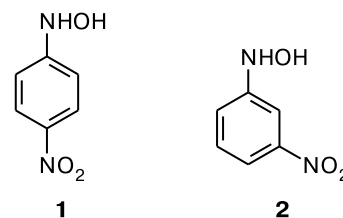
Experimental

Chronoamperometry (CA) and cyclic voltammetry (CV) were carried out on an IPC-Pro-MF computer-controlled potentiostat (Ekoniks, Russia; scan rate inaccuracy 1.0%, potential controller inaccuracy 0.25 mV). Experiments were conducted in a 10-mL five-necked glass conic electrochemical cell with a water jet for temperature maintenance. Polarization curves were recorded using the three-electrode scheme. A glassy carbon electrode (d = 1.7 mm) was used as a working electrode, the platinum wire coil served as an auxiliary electrode, and a saturated calomel electrode (SCE) connected to the solution through a bridge with a porous ceramic membrane filled with a supporting electrolyte (0.1 *M* solution of Bu$_4$NClO$_4$ in DMF) was the reference electrode. The temperature of the studied solutions was maintained at 25±0.5 °C. The solutions were deaerated by passing through them high-purity argon prior to recording each CA and CV curve. Argon was passed above the solution surface to prevent its contact with air during experiment. In the typical experiment, 5 mL of the solution were used. The surface of the

working electrode was polished after each experiment, and the solution was intensively purged with argon.

Since the uncompensated resistance (R_u) substantially affects the result of calculations performed in this work, we attempted a thorough determination of R_u using the CV curves of ferrocene electrooxidation.[5] The value of R_u was calculated from the slope of the potential/current dependence for the anodic and cathodic peaks of the CV curves of 2.5, 5, 10, 15, 20, 25, and 30 *M* solutions of ferrocene at potential scan rates of 0.025, 0.05, 0.1, 0.225, 0.4, 0.65, 1, 2, and 3 V s^{-1}. The obtained dependences turned out to be rigidly linear with a slope corresponding to $R_u = 840 \pm 10$ Ohm. This value is specific for the used working electrode and scheme of electrode arrangement in the cell, which was thoroughly reproduced in each experiment. The exact active surface area of the surface electrode (2.30 mm^2) was determined by the simulation of the CV curves of ferrocene electrooxidation using the known diffusion coefficient of the depolarizer in DMF.[6]

Tetrabutylammonium perchlorate (Acros Organics) and DMF (extra dry grade) were used. The synthesis, isolation, and purification of compound **2** were carried out using a known procedure.[7]

The numerical simulation of the CA and CV curves was performed using the DigiElch Professional, v. 4.0 (build 3.008) software (ElchSoft). The rate constants of the homogeneous reactions were determined from the CA and CV data using an earlier described procedure[2,3] including the variation of the substrate concentration and the potential scan rate. The diffusion coefficients for compound **2** and its RA were accepted to be $1 \cdot 10^{-5}$ cm^2 s^{-1} by analogy with compound **1** for which this parameter was determined previously.[2] The diffusion coefficient for the complexes with the hydrogen bond, whose size approximately two times exceeds that of compound **2**, was estimated by the Stokes—Einstein equation, and its value was $7 \cdot 10^{-6}$ cm^2 s^{-1}. The one-electron ER was considered as electrochemically reversible. and the transfer coefficient (α) was accepted to be 0.5. The standard potentials E°, rate constants (k), and equilibrium constants (K) were determined using an earlier described procedure.[8] The best coincidence of the simulation data with experimental results was achieved with the following set of parameters: $E^\circ_1 = -1.15$ V, $E^\circ_4 = -1.11$ V, $K_2 = 8 \cdot 10^3$ L mol^{-1}, $k_2 = 1 \cdot 10^4$ L mol^{-1} s^{-1}, $K_3 = 1.7 \cdot 10^3$ L mol^{-1}, and $k_3 = 1 \cdot 10^2$ L mol^{-1} s^{-1}.

Results and Discussion

The voltammetric curve of the first step of reduction of compound **2** constructed on the basis of the current of the CA curves in 4 s after feeding a pulse of the indicated potential is shown in Fig. 1. As can be seen at the limiting current potentials the apparent number of electrons n_{app}, equal to the ratio of the experimental current to the theoretical value of the limiting current obtained by numerical simulation for the diffusion process, is close to 1, unlike compound **1** for which $n_{app} = 0.5$ has previously been obtained.[2]

The cathodic (i_c) and anodic (i_a) peaks are observed in the CV curve of compound **2** in the potential range of the described above first wave. The value of n_{app} calculated as the ratio of the experimental peak current i_c to the theoretical one for the process, which is not complicated
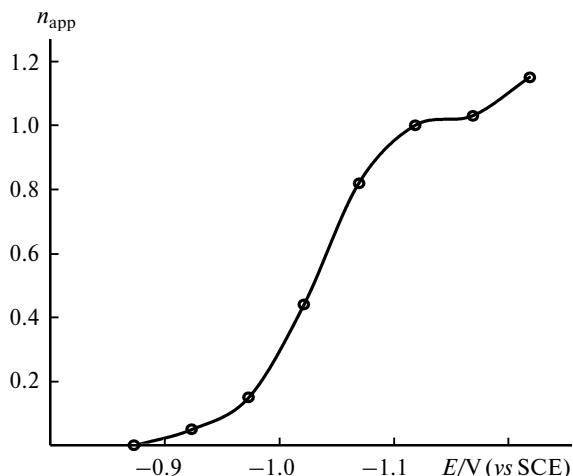
Fig. 1. Voltammetric curve for compound **2** (5 mmol L^{-1}) based in the CA currents in 4 s after feeding a pulse of the indicated potential at the glassy carbon electrode in 0.1 *M* Bu$_4$NClO$_4$/DMF.

by volume reactions, demonstrates a minor increase with a decrease in the concentration (C) and an increase in the potential scan rate (v). As the kinetic parameter λ equal to lg(C/v)[9,10] decreases from -0.5 to -2, n_{app} increases from 0.8 to a limiting value of 0.90 ± 0.02, which is achieved at $\lambda \approx -2$.

As can be seen from Fig. 2, a much more substantial dependence of the ratio of peak currents i_a/i_c in λ is observed with a decrease in λ down to its value about -2. At lower λ, the i_a/i_c ratio stops to depend on this parameter. The latter makes it possible to assume that the RA of compound **2** formed due to the electron transfer enters the second-order reaction, whose products are electrochemically inactive in this range of potentials. On the whole, these results are consistent with the assumption made on
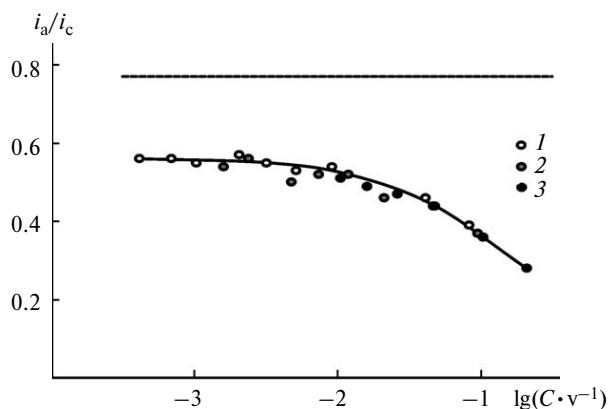

Fig. 2. Ratio of the anodic to cathodic peaks of the CV curves of the ER of compound **2** with concentrations of 2 (*1*), 5 (*2*), and 10 mmol L^{-1} (*3*) in 0.1 *M* Bu$_4$NClO$_4$/DMF *vs* ratio of the concentration and potential scan rate. Dashed line is the simulated value for the diffusion process.

the basis of theoretical data that the rate of the volume reaction of the RA of compound **2** is comparatively low and the volume reactions stop to affect the ER process of compound **2** in the range of low concentrations and high potential scan rates ($\lambda < -2$). However, the values of i_a/i_c observed in this range of λ are significantly lower than the values characteristic of the diffusion process (see Fig. 2).

As shown by the numerical simulation results (Fig. 3), the dependences described above can be observed for the formation of complexes between the depolarizer and product of its reduction

$$\text{ArNHOH} + \text{ArNHOH}^{\cdot -} \underset{k_2, K_2}{\rightleftharpoons} (\text{ArNHOH})_2^{\cdot -}. \qquad (2)$$
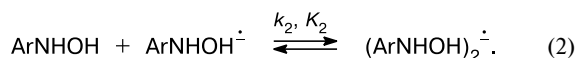
Taking into account the experimental data[11] demonstrating the ability of *N*-phenylhydroxylamines to form hydrogen bonds, it can be assumed that these complexes are formed due to bonds of this type. The formation of this complex between compound **2** and its RA seems most probable, since the equilibrium constants for the reactions of formation of complexes with the hydrogen bond between neutral molecules are many orders of magnitude lower than those for the reactions between the neutral molecule and radical anion.[12] As can be seen from Fig. 3, i_a/i_c depends on the equilibrium constant K_2 of reaction (2) and decreases with its increase. This ratio can also be affected by the formation of a complex between two neutral molecules of depolarizer
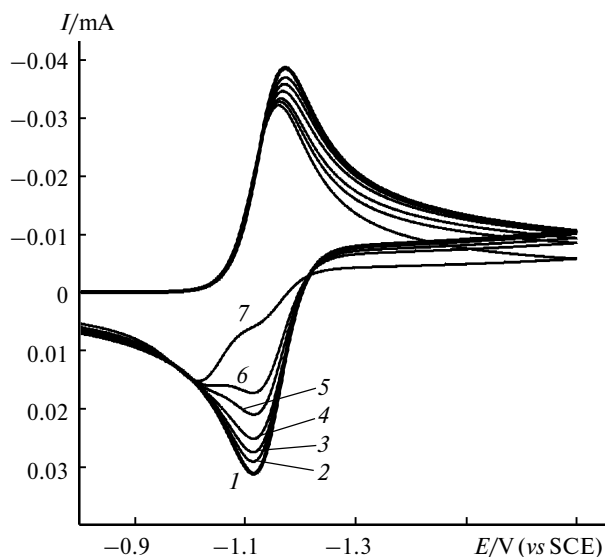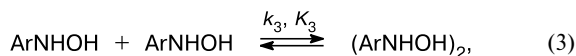
$$\text{ArNHOH} + \text{ArNHOH} \underset{k_3, K_3}{\rightleftharpoons} (\text{ArNHOH})_2, \qquad (3)$$

which should be reduced at more positive potentials than the reduction potential of compound **2**

$$(\text{ArNHOH})_2 \xrightarrow[E^\circ_4]{\text{e}^-} (\text{ArNHOH})_2^{\cdot -}. \qquad (4)$$

In this case, the peak currents should decrease, because the diffusion coefficients of these complexes are lower[13,14] than that of compound **2** because of their large sizes. However, as can be seen from Fig. 4, the i_a/i_c ratio almost should not change.

It is reasonable to assume that complexes of both types can be formed in the system studied and the general mechanism of the ER of compound **2** is described by Eqs (1)—(4). A comparison of the theoretical CV curves calculated for this mechanism with the experimental data (Fig. 5) shows that this mechanism adequately describes indeed the ER process of compound **2** in the range of low concentrations and high potential scan rates ($\lambda < -2$). The parameters of reactions (1)—(4) at which the best coincidence of the theoretical and experimental CV curves is achieved are presented in Experimental. The higher (compared to theoretical values) experimental values of the cathodic current in the potential range lower than -1.3 V are related, most likely, to the further reduction of the complex of compound **2** with its RA. As it is known,[15–19] the formation of hydrogen bonds much more strongly (by hundreds of mV) affects the peak potential corresponding to the transfer of the second electron than the potential of the first potential peak does.

To conclude, the results of the present work confirm the conclusion made on the basis of quantum chemical calculations about a higher stability of the RA of compound

Fig. 3. Theoretical CV curves for the diffusion-controlled process (curve *1*) and the mechanism including reactions (1) and (2): $k_2 = 2000$ L mol^{-1} s^{-1}, $K_2 = 100$ (*2*), 200 (*3*), 400 (*4*), 1000 (*5*), 2000 (*6*), and $1 \cdot 10^{10}$ L mol^{-1} (*7*); $R_u = 0$ Ohm, $v = 1$ V s^{-1}. Other parameters of reactions (1) and (2) are the same as presented in Experimental.
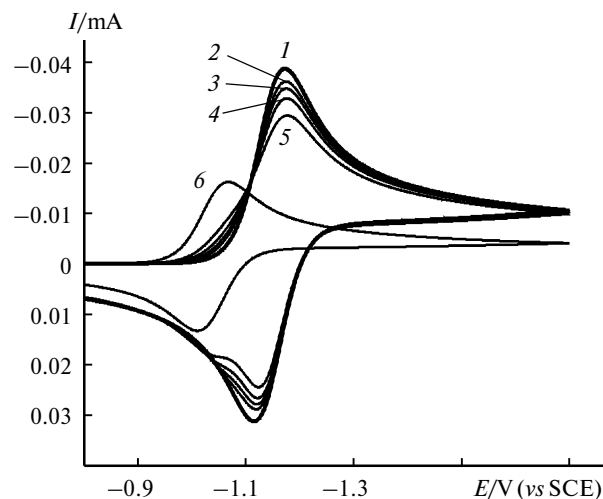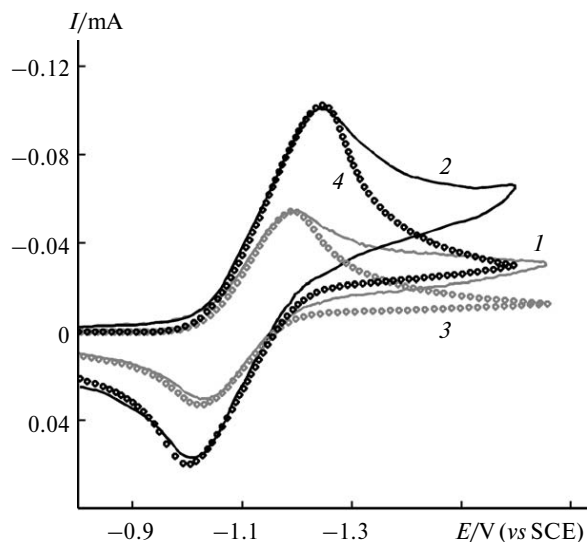

Fig. 4. Theoretical CV curves for the diffusion-controlled process (curve *1*) and the mechanism including reactions (3) and (4): $k_3 = 1 \cdot 10^3$ L mol^{-1} s^{-1}, $K_3 = 10$ (*2*), 20 (*3*), 40 (*4*), 100 (*5*), and $1 \cdot 10^{10}$ L mol^{-1} (*6*); $R_u = 0$ Ohm, $v = 1$ V s^{-1}. Other parameters of reactions (1) and (2) are the same as presented in Experimental.

Fig. 5. Experimental (*1*, *2*) and theoretical (*3*, *4*) cyclic voltammetry curves for compound **2** with concentrations of 2 (*1*, *3*) and 5 mmol L^{-1} (*2*, *4*); $v = 3$ V s^{-1}, $R_u = 860$ Ohm. The parameters used for the calculation of the theoretical curves are given in Experimental.

2 compared to its isomers and show that in a range of low concentrations and high scan rates the ER of compound **2** is complicated only by processes of formation of complexes between the depolarizer molecules, as well as between the depolarizer and its radical anion, most likely, due to hydrogen bonds.

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