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Self-protonation upon the electroreduction of 2- and 4-nitrophenylhydroxylamines in aprotic media

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Cyclic voltammetry and controlled potential electrolysis were used to show that radical anions of 2- and 4-nitrophenylhydroxylamines electrochemically generated in a 0.1 M Bu_4NClO_4 solution in DMF undergo protonation with the starting compounds (self-protonation) followed by the formation of the corresponding nitroanilines.

A typical reaction of organic radical anions (RAs) is their protonation, which is a result of a considerable increase in their basicity compared to the starting compound due to an excessive electron on the high-lying frontier molecular orbital.[1] Since the rate constant of RA protonation increases with decreasing the difference in energies of the frontier molecular orbitals of the RA and the proton donor, in the degenerate case, when the initial neutral molecule acts as a proton donor, the proton can be transferred even if the proton-donor ability of this molecule is comparatively low. This reaction named 'self-protonation' was observed earlier for some classes of compounds,[2,3] including nitroaromatic ones, for example, nitrophenols.[4–8] This reaction was not described for the *N*-phenylhydroxylamine derivatives (which are significant as intermediates of reduction of the nitrobenzene derivatives[9]), although the latter, as known, can act as NH and OH acids.[10] We studied the near-electrode reactions of RA of 2- and 4-nitrophenylhydroxylamines (2- and 4-NPHA) in a 0.1 M solution of Bu_4NClO_4 in DMF.†

The cyclic voltammetry (CV) curves of 4-NPHA are presented in Figure 1. The cathodic branch of the curve exhibits two peaks at potentials of –1.23 (P1) and –1.45 V (P2).‡ The first peak (P1) is chemically irreversible, and its current is appreciably lower than the theoretical value for the one-electron process.§ The potential of the second reversible peak (P2) corresponds

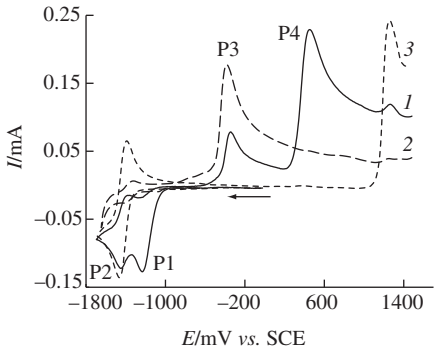

Figure 1 Cyclic voltammograms in DMF containing 0.1 M Bu_4NClO_4 at the carbositall electrode (d = 3 mm) and a potential sweep of 0.1 V s^{-1} (T = 298 K): 15 mM 4-NPHA in the absence (*1*) and in the presence of 15 mM Et_4NOH (*2*), 8 mM 4-NA (*3*).

† Synthesis and purification of 2- and 4-NPHA were carried out according to a known procedure.[11]

‡ Potentials were measured *vs.* the KCl saturated calomel electrode (SCE) connected with the studied solution through a salt bridge, which was filled with the supporting electrolyte (0.1 M Bu_4NClO_4 solution in DMF).

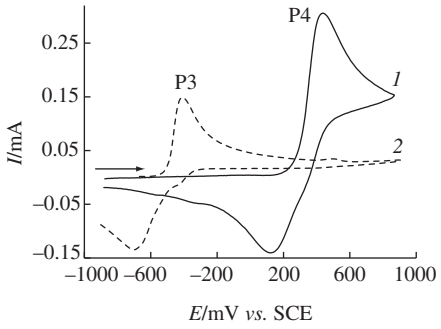

Figure 2 Cyclic voltammograms in DMF containing 0.1 M Bu_4NClO_4 at the carbositall electrode (d = 3 mm) and a potential sweep of 0.1 V s^{-1} (T = 298 K): 15 mM 4-NPHA in the absence (*1*) and in the presence of 15 mM Et_4NOH (*2*).

to that of the peak of 4-nitroaniline (NA) formed upon the electroreduction of 4-NPHA in the presence of proton donors.

The anodic branch of the CV curve of 4-NPHA contains the peak at a potential of –0.34 V (P3) corresponding to the oxidation of the 4-NPHA anion. This assignment was made by the behavior of 4-NPHA solutions containing the base. The addition of Et_4NOH results in a change in the solution color to bright red, which is characteristic of the 4-NPHA anions.[11] In this case, the current of the above anodic peak (P3) increases, and the heights of the cathodic peaks corresponding to 4-NPHA (P1) and 4-NA (P2) reduction decrease. The anodic peak at 0.43 V of the 4-NPHA oxidation (P4) disappears (Figure 2) simultaneously with an increase in the current of 4-NPHA anion peak (P3).

Thus, the 4-NPHA anion is formed in the presence of the base both added to the solution and cathodically generated the 4-NPHA RA. Taking into account that the current of the first cathodic peak (P1) is underestimated compared to the one-electron process, which is because of the interaction of the reduction product (RA) with the starting 4-NPHA, we can suggest that self-protonation occurs. The overall mechanism of the process can be described by the ECE scheme taking into account that the starting compound 4-NPHA (R = 4-$NO_2C_6H_4$) acts as a proton donor:

$$RNHOH \xrightarrow{e^-} RNHOH^{\cdot -} \quad (1)$$

$$RNHOH^{\cdot -} + 2RNHOH \xrightarrow[-H_2O]{e^-} RNH_2 + 2RNOH^- \quad (2)$$

§ This is seen as from the comparison of the CV curves for 4-NPHA and 4-NA, so by determination of the diffusion coefficient of 4-NPHA by the peak of its oxidation, and calculation of the theoretical one-electron level.

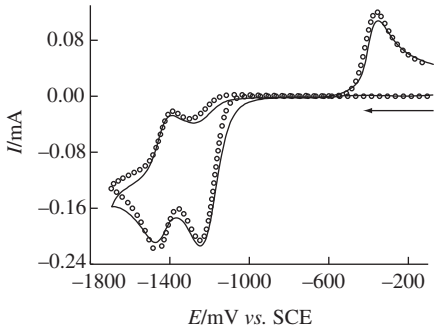

Figure 3 Cyclic voltammogram of 25 mM 4-NPHA in DMF containing 0.1 M Bu_4NClO_4 at the carbositall electrode (d = 3 mm) and a potential sweep of 0.1 V s^{-1} (T = 298 K) (line). Empty circles show corresponding simulated curves for self-protonation of 4-NPHA with formation of 4-NA and 4-NPHA anion.

The simulation of the CV curves (Figure 3) using this scheme results in the satisfactory agreement between the experimental and calculated data.¶ We used the value of the formation potential of first electron transfer, which was estimated from the electron affinity of 4-NPHA calculated by the density functional theory (DFT) using the B3LYP exchange-correlation functional and the correlation dependence obtained earlier.[13]

The electroreduction of 2-NPHA is analogous to the above-described behavior of 4-NPHA. The cathodic branch of the CV curve for 2-NPHA (Figure 4) exhibits two peaks at –1.10 (P1′) and –1.30 V (P2′). As in the case of 4-NPHA, the first of these peaks corresponds to the chemically irreversible reduction of 2-NPHA, and the second peak corresponds to the reversible reduction of 2-NA. The anodic branch of the curve contains a peak at –0.33 V (P3′) corresponding to the oxidation of the 2-NPHA anion. The reduction curves of 2-NPHA reduction in the presence of Et_4NOH are also shown in Figure 4.

For the additional identification of the reduction products, we carried out electrolyses of 2- and 4-NPHA at the potentials of the limiting current of the first electroreduction waves for these compounds.

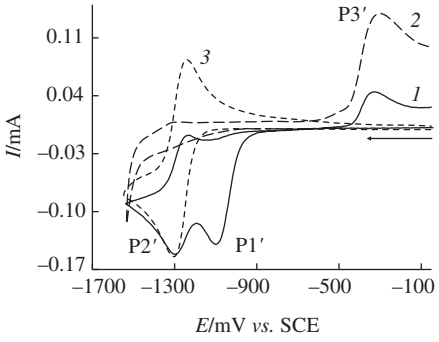

Figure 4 Cyclic voltammograms in DMF containing 0.1 M Bu_4NClO_4 at the carbositall electrode (d = 3 mm) and a potential sweep of 0.1 V s^{-1} (T = 298 K): 15 mM 2-NPHA in the absence (*1*) and in the presence of 15 mM Et_4NOH (*2*), 8 mM of 2-NA (*3*).

¶ The CV curves were simulated using the DigiElch Professional program (ElchSoft), v. 3 (Build 3.600).[12] Mechanism used for the simulation involved the following successive stages: electron transfer – protonation – electron transfer – protonation – water molecule elimination resulted in 4-NA formation. Since investigation of 4-NA reduction was beyond the scope of this work, it was supposed for simplicity that degradation of 4-NA anion radical is a pseudo-first-order reaction. The limiting stage was the first proton transfer ($k_p = 3\times10^3$ dm^3 mol^{-1} s^{-1}), and rate constant for 4-NA anion radical degradation was 0.25 s^{-1}. Other simulation parameters: $E^{0\prime}_{red\ 4\text{-NPHA}} = -1.26$ V, $E^{0\prime}_{ox\ 4\text{-NPHA}} = 0.44$ V, $E^{0\prime}_{ox\ 4\text{-NPHA anion}} = -0.40$ V, $E^{0\prime}_{red\ 4\text{-NA}} = -1.43$ V, T = 298.15 K, $D_{4\text{-NPHA}} = 6\times10^{-6}$ cm^2 s^{-1}, $D_{4\text{-NA}} = 1\times10^{-5}$ cm^2 s^{-1}, k_s = 1 cm s^{-1}, α = 0.5.

The exhaustive electrolysis of 4-NPHA occurred with the consumption of 0.43 electron per substrate molecule, which is somewhat lower than 0.66, which corresponds to the stoichiometry of reactions (1) and (2). During the electrolysis, the solution turned bright red, which is characteristic of the 4-NPHA anion.[11] After the electrolysis completed, the CV curves of the catholyte contained peak corresponding to the reduction of 4-NA and oxidation of 4-NPHA anion, and no reduction and oxidation peaks of the 4-NPHA.

The acidification of the catholyte with a phosphate buffer (pH 3), as shown by HPLC analysis,†† was accompanied by 4-NPHA regeneration in an amount of 49% of its initial amount due to the protonation of the 4-NPHA anion. According to the HPLC data, the yield of 4-NA was 20%. Thus, the products of 4-NPHA electrolysis correspond to the products of reaction (2).

The fact that the yields of the 4-NPHA anion and 4-NA are noticeably lower than the theoretical values, which for this process should be 66 and 33%, respectively, indicates that side reactions occur during the electrolysis. Unlike the CV method, whose time window is measured in seconds, the time necessary for the exhaustive electroreduction (tens of minutes) is sufficient for the contribution of side reactions to become appreciable. The most probable reactions decreasing the product yield are those of the 4-NPHA anion with the solution components, including 4-NPHA itself.

The electrolysis of 2-NPHA at the potentials of the limiting current of the first reduction step is accompanied by the appearance of a bright violet color characteristic of the 2-NPHA anion.[11] The yields of the 2-NPHA anion and 2-NA were 49 and 30%, respectively, based on the starting 2-NPHA.

Thus, we can conclude that the electroreduction of both 2- and 4-NPHA at the potentials of the first step proceeds *via* the mechanism including the step of RA protonation with the starting compound and affords NA and the NPHA anion.

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†† HPLC was carried out on a Diasfer-110-S16 column (5 μm, 2.0×80 mm) using a MeCN/0.1 M phosphate buffer mixture with pH 3 in a ratio of 25:75 as a mobile phase and an UV detector at wavelengths of 235 (2-NA) and 350 nm (4-NA, 2- and 4-NPHA).