Electroreduction of primary nitramines on platinum in MeCN

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Reduction of primary nitramines $RNHNO_2$ (R = Me, Et, Pr^i, α-pyridyl) in anhydrous MeCN at a Pt cathode was studied by voltammetry and electrolysis. The process includes one-electron transfer and nitramine deprotonation to give the corresponding anions. The products of *N*-alkylation of these anions can be obtained only when their potassium salts are used (but not tetrabutylammonium salts). This is due to the effects of ion association, which influence the dual reactivity of the anions under investigation.

Key words: primary nitramines, electroreduction, cathodic deprotonation, ion association.

Data on the cathodic behavior of nitramines in nonaqueous media are scarce and largely refer to processes occurring at a mercury cathode. Polarographic reduction of secondary nitramines in DMF (see, for example, Ref. 1) can be described by the following scheme:

$$>N{-}NO_2 + 2\,\bar{e} \longrightarrow\ >N^- + NO_2^-.$$

Only few communications are devoted to reduction of primary nitramines under these conditions. Thus, according to published data,[2] the mechanism of electroreduction of primary nitramines includes the step of "self-protonation" of the intermediate amide anion, according to the following scheme:

$$\begin{array}{l}
RNHNO_2 + \bar{e} \longrightarrow RNHNO_2^{\cdot -}\\
RNHNO_2^{\cdot -} \longrightarrow R\dot{N}H + NO_2^-\\
R\dot{N}H + \bar{e} \longrightarrow R\bar{N}H\\
RNHNO_2 + R\bar{N}H \longrightarrow RNH_2 + R\bar{N}NO_2\\
\hline
2\,RNHNO_2 + 2\,\bar{e} \longrightarrow RNH_2 + R\bar{N}NO_2 + NO_2^-, \qquad (1)
\end{array}$$

In the presence of excess proton donors (*e.g.*, PhOH), this formally single-electron process becomes a two-electron process,

$$RNHNO_2 + 2\,\bar{e} \xrightarrow{PhOH} RNH_2 + NO_2^-,$$

which is consistent with the twofold increase in the height of the polarographic wave of primary nitramines.[2]

Thus, it follows from the results of the studies cited[1,2] that reduction of both secondary and primary nitramines in nonaqueous media at a mercury cathode is accompanied by cleavage of the N—N bond, resulting in the elimination of the NO_2^- ion.

To continue our previous studies[3] taking account of the above data, in this communication we studied the characteristic features of electroreduction of a number of primary nitramines at a platinum cathode in anhydrous MeCN.

The second reason that prompted us to carry out this study should also be mentioned. The numerous examples of electrosynthesis considered in a review[4] indicate that the reduction of various organic acids at a Pt cathode in aprotic media is accompanied by their deprotonation with generation of the corresponding anions. It has been of interest to obtain direct voltammetric evidence for the occurrence of this process. In this respect, primary nitramines are very convenient models, because they are N—H acids and contain an NO_2 group, which is one of the most readily reducible groups.

Results and Discussion

According to published data,[5] the polarograms of primary nitramines in aqueous solutions show reduction waves for the equilibrium tautomeric forms of these compounds, whereas the polarograms of these compounds recorded in DMF exhibit only one wave due to reduction of the nitro form.[2] In conformity with this finding,[2] we have shown that the polarization curves of the primary nitramines $RNHNO_2$, where R = Me (**1**), Et (**2**), Pr^i (**3**), and α-pyridyl (**4**), recorded using a rotating platinum disk electrode in anhydrous MeCN each exhibit one reduction wave (Fig. 1) with close limiting current values.

In the anodic potential range, for primary nitramines, only a weak current increase is most often observed (at *E* = 1.5 to 2.0 V, see Fig. 1), and voltammograms nearly coincide with the background curve. This may be due to the passivation of the electrode surface by oxidation

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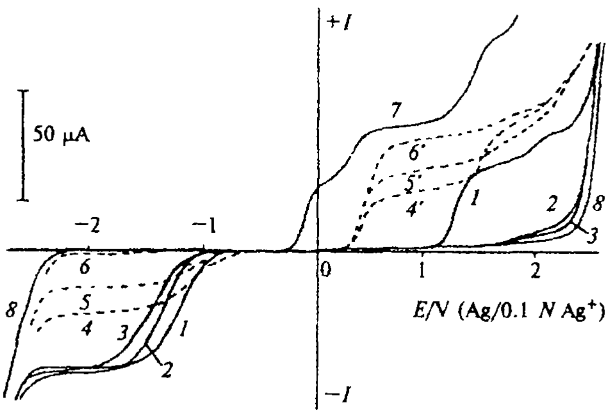

Fig. 1. Voltammetric behavior of α-pyridyl- (*1*), ethyl- (*2*), and isopropylnitramines (*3*) ($C = 5 \cdot 10^{-3}$ mol L^{-1}); the decrease in the reduction wave of α-pyridylnitramine during electrolysis ($E = -1.8$ V) (*4*—*6*) and the simultaneous appearance of the oxidation wave for its anion (*4'*—*6'*, respectively); the voltammogram obtained after addition of methyl iodide to a solution of α-pyridylnitramine subjected to electrolysis (*7*). Curve *8* shows the background current (rotating Pt disk electrode, MeCN, 0.1 *N* Bu_4NClO_4).

products.* This distinguishes the primary alkylnitramines considered here from the corresponding secondary derivatives, whose oxidation waves, according to the published data,[6] are characterized by $E_{1/2}$ values of 0.8—1.2 V. The only exception is nitramine **4**, for which the oxidation wave is also clearly defined (see Fig. 1).

The heights of the cathodic waves of nitramines **1**—**4** increase linearly upon an increase in the depolarizer concentration in the $2 \cdot 10^{-3}$—$2 \cdot 10^{-2}$ mol L^{-1} range, and their dependence on the electrode rotation rates shows the diffusion nature of waves. The $E_{1/2}$ values for these waves change noticeably only on passing from compounds **1**—**3** with electron-donating substituents at the nitrogen atom to nitramine **4** with an electron-withdrawing substituent (Table 1). The number of electrons (*n*) consumed at the stage of nitramine reduction, determined by coulometry, varies from 0.7 to 1.0 depending on the nature of the nitramine. Thus, one can conclude that the reduction of nitramines under the experimental conditions is a one-electron process.

To elucidate the regularities of this process, we carried out controlled-potential microelectrolysis at the plateau of the nitramine reduction waves and then carried out voltammetric analysis of the resulting products. The study showed that passing 1 F of electricity per mole of nitramine results in exhaustive electrolysis leading to disappearance of the reduction wave of nitramine and simultaneous appearance and growth of several anodic waves. The shapes and potentials of these waves are identical to those of the waves observed for the oxidation of the corresponding nitramine anions (Fig. 2). Thus, it can be concluded that reductive electrolysis of nitramines results in the generation of the corresponding anions.

Table 1. Voltammetric characteristics ($E_{1/2}$/V) of primary nitramines ($RNHNO_2$), products of their cathodic electrolysis ($E = -1.8$ V), and nitramine anions ($RNNO_2^-$)

R	$RNHNO_2$		Electrolysis products		$RNNO_2^-$	
	$E_{1/2}^{red}$	$E_{1/2}^{ox}$	$E_{1/2}^{ox1}$	$E_{1/2}^{ox2}$	$E_{1/2}^{ox1}$	$E_{1/2}^{ox2}$
Me	−1.37	—	0.63	1.12	0.61	1.1
Et	−1.40	—	0.67	1.15	0.63	1.1
Pr^i	−1.50	—	0.71	—	0.67	—
α-py	−1.20	1.25	0.42	1.85	0.40	1.76

Note. The $E_{1/2}$ values are given *vs* Ag/0.1 *N* Ag^+, a rotating Pt disk electrode, MeCN, 0.1 *N* Bu_4NClO_4, $C = 5 \cdot 10^{-3}$ mol L^{-1}.

In principle, this process could be described in terms of the previously proposed scheme.[2] In this case, judging by overall Eq. (1), after 2 F of electricity have been passed, cathodic electrolysis of primary nitramines gives the nitrite ion, the nitramine anion, and alkylamine, which are produced in equal amounts. However, it was found that when 1 F of electricity per mole of nitramine has been passed, the cathodic waves of nitramines **1**—**4** completely disappear, whereas according to the scheme presented above, they would only decrease by 50%.

In this respect, cathodic microelectrolysis of nitramine **4**, which is active in both the anodic and cathodic potential regions, is an illustrative example. Passing of

Fig. 2. Voltammograms recorded during the cathodic electrolysis ($E = -1.8$ V) of ethylnitramine ($C = 7.5 \cdot 10^{-3}$ mol L^{-1}) (*1*—*3*); oxidation waves for tetraethylammonium ethylnitraminate ($C = 2.8 \cdot 10^{-3}$ mol L^{-1}) (*4*) and for the nitrite ion ($C = 3 \cdot 10^{-3}$ mol L^{-1}) (*5*). Curve *6* shows the background current (MeCN, 0.1 *N* Bu_4NClO_4).

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* Passivation effects often accompany both voltammetric studies and electrolysis of nitramines. The passivation can be eliminated (not always) by the reverse of the potential to the region with the opposite polarity or by choosing an appropriate supporting electrolyte.

1 F of electricity per mole of compound **4** results in a gradual decrease of its cathodic and anodic waves (they entirely vanish at the end of the electrolysis). Simultaneously, an oxidation wave for the corresponding anion* with $E_{1/2}$ = 0.4 V appears and grows (see Fig. 1). Note that both species formed according to overall Eq. (1), NO_2^- and $RNNO_2^-$, are electrochemically active in the anodic range of potentials. However, none of the polarization curves of oxidation of the reaction mixtures obtained after exhaustive reductive electrolysis of nitramines **1—4** exhibited an oxidation wave for the nitrite ion, which would occur at ~0.3 V (see Fig. 2), although, in conformity with the scheme considered here, this species would have formed in an equimolar amount in relation to the nitramine anion. Moreover, as noted above, the shapes, the $E_{1/2}$ values, and the height ratios of the waves detected on the anodic polarization curve of the reaction mixture obtained after reductive electrolysis of nitramines **1—4** coincide with those for the oxidation waves observed for the specially prepared nitramine anions (see Fig. 2 and Table 1). The data obtained lead to the conclusion that the cathodic electrolysis of primary nitramines **1—4** under the experimental conditions gives only the corresponding anions. In this case, the mechanism of the process should be represented as follows:

$$RNHNO_2 + e \xrightarrow[-1/2\,H_2]{} RNNO_2^- . \qquad (2)$$

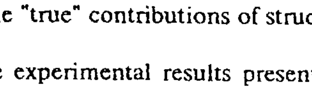
We proposed this mechanism[4] when considering numerous examples of electroorganic synthesis, which point to the occurrence of cathodic deprotonation of organic acids. Now this mechanism has received additional evidence based on the data of voltammetry and microelectrolysis of primary nitramines. It can be suggested that the electron transfer (Eq. (2)) occurs with partial binding between the platinum cathode surface and the hydrogen atom at the amine center (unlike mercury, platinum efficiently adsorbs atomic hydrogen). Simultaneously, the bonds formed by nitrogen atoms become partly double, which is typical of the anionic structures of primary nitramines.

Previously we showed[4] that it is possible, in principle, to carry out electrochemical alkylation of primary nitramines during their deprotonation under reductive electrolysis conditions. The study of this process that we report here provided additional information. Thus addition of MeI to the catholyte after electrolysis of primary alkylnitramines results in gradual disappearance of the oxidation waves of the nitramine anions appearing during electrolysis on the voltammograms. Simultaneously, oxidation waves for the iodide ion (the first two waves) and the alkylated product (the third wave) appear (see Fig. 1, curve *7*).

It is known that nitramine anions are weak nucleophiles and their reaction with alkyl halides may take several days.[8] For this reason, we did not optimize the experimental conditions but chose a 20-hour stirring of the reaction mixture after electrolysis with excess MeI at room temperature as the standard procedure.

We found that the efficiency of the alkylation depends substantially on the nature of the cation of the supporting electrolyte. For instance, after potentiostatic electrolysis ($E = -1.7$ V, 1 F per mole of nitramine) of compounds **1—3** with 0.1 *N* Bu_4NClO_4 as the supporting electrolyte and stirring of the resulting solution with excess MeI, we were unable to isolate the corresponding methyl-substituted (secondary) nitramines from the reaction mixture. However, when Bu_4N^+ in the supporting electrolyte was replaced by K^+, electrolysis under the same conditions afforded secondary nitramines in 35—55% yields based on the initial nitramine. In our opinion, this effect is due, on the one hand, to the ambident properties of the intermediate N-anion caused by the known tautomerism in the primary *N*-nitramine series,[9] and, on the other hand, to the ability of the supporting cations to form ion associates of various strengths, depending on the cation nature.

According to published data,[7] the state of the primary nitramine anions in solution can be described by two canonical resonance structures **A** and **B** and the contribution of structure **B** predominates:



A **B**

It can be assumed that in the presence of alkali metal cations, in particular K^+, which is coordinated to the oxygen atoms of the anion, fairly stable associates are formed; apparently, this increases the nucleophilicity of the amine nitrogen atom. Conversely, in the presence of the Bu_4N^+ cation, which does not tend to form ion associates, the "true" contributions of structures **A** and **B** are retained.

Thus, the experimental results presented above can be explained by assuming that nucleophilic substitution involving tetraalkylammonium salts of nitramines gives *O*-methylated products. They are known for their instability[9] and must decompose during workup of the reaction mixture. Conversely, nucleophilic substitution with participation of the nitramine potassium salts yields stable *N*-alkylated products.

The results obtained can be summarized by stating that electrochemical reductions of primary nitramines at Hg and Pt cathodes obey different rules: in the former case, this process is accompanied by cleavage of the

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* In addition to the wave with $E_{1/2}$ = 0.4 V, the voltammogram has a small second wave at −1.55 V (see Fig. 1). Similar waves are also noticed on the oxidation curve for the anion of **4** (the tetrabutylammonium salt). The potential of the second wave depends on the anion concentration; most likely, its nature is caused by the oxidation of the nonionized form of **4**, which arises upon abstraction of a hydrogen atom from a medium component by the N-centered radical, formed at the first ($E_{1/2}$ = 0.4 V) step of oxidation of the anion of **4**.

N—N bond, whereas in the latter case, it involves cleavage of the N—H bond. Using nucleophilic substitution as an example, it was found that the reactivity of ambident anions of nitramines depends appreciably on the nature of the counter-ion. This is due to the formation of ion associates with different strengths, and, as a consequence, by the change in the electron density distribution in the anionic reagent.

Experimental

Voltammetric measurements were carried out in a glass cell with a porous glass diaphragm at a constant temperature of 25±0.1 °C. A rotating platinum disk electrode (S = 7.61 cm^2) was used as the cathode, a graphite rod was used as the anode, and the reference electrode was the Ag/0.1 N Ag$^+$ system. The potential was applied using a P-5227M potentiostat. A 0.1 N solution of Bu_4NClO_4 in anhydrous MeCN was used as the supporting electrolyte.

Prior to the recording of polarization curves and electrolysis, the working solution was deaerated by a flow of argon.

Controlled-potential electrolysis (−1.7 to −1.9 V) was carried out in a hermetically sealed cell of the same design but of a larger volume. Platinum (S = 28 cm^2) was the cathode, and the catholyte volume was 120 mL; a graphite rod was the anode, and the anolyte volume was 40 mL. A 0.1 N solution of Bu_4NClO_4 or a 0.1 N solution of $KClO_4$ in anhydrous MeCN was used as the supporting electrolyte.

For electrolysis, 10 mmol of the nitramine studied was placed in the cathode area of the electrolyzer. The amount of the nitramine anion formed was determined by the limiting current of the oxidation wave using the calibration plot of current *vs* concentration for the authentic anion of the corresponding nitramine.

Secondary nitramines. After electrolysis, a twofold excess of MeI (based on the initial nitramine) was added to the solution. After the reaction mixture had been stirred for 20 h at –20 °C, 500 mL of diethyl ether was added, and the mixture was washed with water (4×100 mL). The organic layer was dried with anhydrous $MgSO_4$, the ether was evaporated under atmospheric pressure, and the residue was distilled *in vacuo*. The resulting *N,N*-dialkylnitramines were identified by IR and ^{1}H NMR spectroscopy and mass spectrometry.

Primary nitramines 1—4 were synthesized by known procedures.[10—12] The tetrabutylammonium salts of these nitramines were prepared by alkalization of their methanolic solutions with an equimolar amount of potassium hydroxide followed by the addition of the calculated amount of tetrabutylammonium perchlorate. After precipitation of the alkali metal salt by acetone, the filtrate was concentrated *in vacuo*, and the residue was crystallized from organic solvents.

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