Electrooxidation of primary nitramine anions on platinum in MeCN

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Oxidation of primary nitramine anions $RNNO_2^-Bu_4N^+$ (R = Me, Et, Pr^i, or methoxyfurazanyl) in 0.1 *N* Bu_4NClO_4 in MeCN on a Pt anode was studied by voltammetry and controlled potential electrolysis. It was found that the first stage of oxidation affords the corresponding radicals, which are further stabilized due to hydrogen abstraction from the medium. These radicals are also involved in other reactions, including those, which yield azo derivatives. The possibility of generation of nitrene species in these reactions is discussed.

Key words: electrooxidation of nitramine anions, nitrenes, azo compounds.

Previously,[1] we examined the possibility of cathode deprotonation of primary nitramines. As part of continuing studies of the electrochemical behavior of nitramines, in the present work we studied the regularities of electrooxidation of nitramine anions containing a donor or acceptor substituent at the amine nitrogen atom. Judging from the published data, these processes are still poorly understood. However, radical intermediates, which are probable intermediates in the oxidation of nitramine anions, could be considered as potential sources of nitrene species.

Experimental

The voltammetric measurements were carried out in a temperature-controlled (25 °C) glass cell with cathode and anode compartments separated by a porous-glass filter. The polarization curves were recorded on a rotating disk Pt electrode ($7.61 \cdot 10^{-3}$ cm^2) using a P-5827M potentiostat. A graphite rod was used as the auxiliary electrode and Ag/0.1 *N* $AgNO_3$ was used as the reference electrode.

The coulometric measurements and microelectrolysis were carried out in the same cell. A platinum plate (2 cm^2) was used as the working electrode, but the polarization curves were recorded in the course of electrolysis using a rotating disk Pt electrode.

The preparative electrolysis was performed in a sealed cell analogous to that described above (but of a larger volume). A Pt plate (28 cm^2) was used as the anode. The auxiliary and reference electrodes were the same as those used in the voltammetric measurements.

A 0.1 *N* Bu_4NClO_4 solution in anhydrous MeCN was used as the supporting electrolyte in the voltammetric measurements and in the electrolysis. The working solution was deaerated with argon before the polarization curves were recorded and the electrolysis was performed.

Dehydration of MeCN was performed by distillation over P_2O_5 (five times) followed by distillation over calcined K_2CO_3.

Methyl-, ethyl-, and isopropylnitramines were prepared according to procedures reported previously.[2,3] Tetrabutylammonium salts of the above-mentioned nitramines were prepared by adding an equimolar amount of KOH to their methanolic solutions followed by cation exchange upon addition of the calculated amount of tetrabutylammonium perchlorate. The alkali salts were precipitated with acetone, the filtrates were concentrated *in vacuo*, and the residues were recrystallized from organic solvents. 4-Amino-3-methoxyfurazan was prepared according to a known procedure.[4] A procedure, which we have specially developed for the preparation of the tetrabutylammonium salt of 3-methoxy-4-*N*-nitraminofurazan (MNAF), is described below.

The ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument. The IR spectra were recorded on a Specord 75-IR instrument. The course of the reactions was monitored by TLC on Silufol UV-254 plates.

Tetrabutylammonium salt of 3-methoxy-4-*N*-nitraminofurazan (MNAF). 4-Amino-3-methoxyfuran (3.8 g, 33 mmol) was added with stirring to nitric acid (5 mL; *d* = 1.5) at a temperature from −5 to −15 °C. The reaction mixture was kept for 40 min and then added to a cooled (−5 °C) solution of KOH (10 g, 179 mmol) in water (150 mL). A solution of Bu_4NBr (30 g) in water (250 mL) was added to the reaction mixture and the solution was heated to 90 °C and filtered. The filtrate was cooled to room temperature. The crystals that precipitated were separated on a filter and washed with cold water (3×50 mL). The tetrabutylammonium salt of MNAF was obtained in a yield of 9 g (67.9%), m.p. 103 °C. Found (%): C, 56.83; H, 9.79; N 17.44. $C_{19}H_{39}N_5O_4$. Calculated (%): C, 56.87; H, 9.40; N, 17.98. IR (KBr), ν/cm^{-1}: 3440 br, 2970 m, 2960 w, 2910 w, 2880 m, 1595 m, 1505 s, 1465 m, 1440 m, 1415 m, 1515 w, 1265 s, 1190 w, 1165 w, 1110 w, 1060 w, 1035 w, 990 m, 910 w, 880 w, 845 w, 795 m, 740 m, 700 w. ^{1}H NMR (acetone-d$_6$), δ: 0.95 (t, 12 H, CH_3, *J* = 7.5 Hz); 1.40 (qt, 8 H, CH_2, *J* = 7.5 Hz); 1.79 (m, 8 H, CH_2); 3.43 (m, 8 H, NCH_2); 3.96 (s, 3 H, OCH_3).

Electrochemical synthesis of 3,3′-dimethoxyazofurazan (DMAF). The tetrabutylammonium salt of MNAF (3.46 g, 8.62 mmol) in a 0.2 *N* Bu_4NClO_4 solution in dry MeCN (85 mL) was placed into the anode compartment of an elec-

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trochemical cell. Electrolysis was carried out at a controlled potential (1.2 V) using a Pt plate (28 cm^2) as the anode. Then 1 F per mole of the initial anion was passed through the reaction mixture and the mixture was diluted with diethyl ether (500 mL) and washed with water (4×100 mL). The ethereal solution was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel L = 40/100 m (benzene as the eluent, R_f = 0.59). 3,3'-dimethoxyazofurazan was obtained in a yield of 0.42 g (21%). Based on the data of TLC, IR and NMR spectroscopy, and m.p., the specimen is identical to the known specimen of 3,3'-dimethoxyazofurazan.[4]

Results and Discussion

Depending on the structure of nitramine anions, two or three waves of different heights are observed on polarization curves during their oxidation (Figs. 1—3, curves *1*). Thus, there are three anodic waves with $E_{1/2}$ = 0.61, 1.1, and 1.7 (Fig. 2) and with $E_{1/2}$ = 0.63, 1.1, and 1.7 V on the polarization curves of methylnitramine (MNA) and ethylnitramine (ENA), respectively. The values of $E_{1/2}$ are shifted to the positive-potential region by ≥100 mV as the concentration of MNA increases in the range of 2—20 · 10^{-3} mol L^{-1}. The limiting currents at the potentials of the first and second waves increase proportionally to the concentration. However, the ratio between the heights of the first two waves varies from ~4.5 to 3, *i.e.*, the height of the second wave increases faster than that of the first wave as the concentration increases. The linear dependence of the limiting currents of the first and second waves on the square root of electrode rotation speed shows the diffuse character both of the first and overall (first and second) oxidation waves on the polarization curves of the MNA and ENA anions. The coulometric measurements at the potentials of the first waves gave n ~1 e.

Unlike the above-considered anions, only two waves with $E_{1/2}$ = 0.67 and 1.7 V are observed on the polarization curve of oxidation of the isopropylnitramine (IPNA) anion (see Fig. 1, curve *1*). The values of $E_{1/2}$ for these waves are also shifted to the anodic-potential region as the concentration increases. The first oxidation wave of the IPNA anion is also diffuse in character. According to the coulometric data, the limiting current of the latter

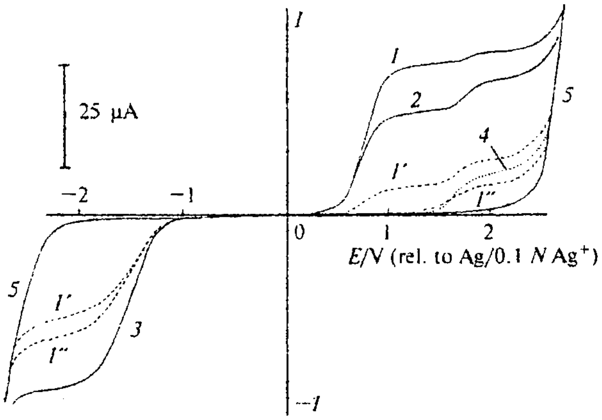


Fig. 1. Voltammograms recorded on a rotating disk Pt electrode: *1*, *1'*, and *1''*, the voltammograms recorded before, in the course of, and after microelectrolysis, respectively, of the tetrabutylammonium salt of IPNA (C = 4.2 · 10^{-3} mol L^{-1}) on a stationary Pt electrode (S = 2 cm) in a 0.1 N Bu_4NClO_4 solution in anhydrous MeCN at the potential E = 1.5 V; *2*, the voltammogram of the final solution subjected to complete reduction at the potential E = −1.8 V; *3* and *4*, the voltammograms of IPNA (C = 1.7 · 10^{-3} mol L^{-1}) and Bu_4NNO_3 (C = 3 · 10^{-3} mol L^{-1}) in the supporting solution, respectively; *5*, current of the supporting-solution.

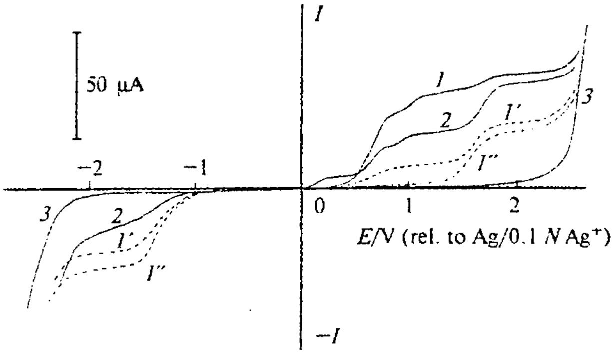


Fig. 2. Voltammograms recorded on a rotating disk Pt electrode: *1*, *1'*, and *1''*, the voltammograms recorded before, in the course of, and after microelectrolysis, respectively, of the tetrabutylammonium salt of MNA (C = 7.1 · 10^{-3} mol L^{-1}) on a stationary Pt electrode (S = 2 cm) in a 0.1 N Bu_4NClO_4 solution in anhydrous MeCN at the potential E = 1.4 V; *2*, the voltammogram of the final solution in the course of its reduction at the potential E = −1.5 V; *3*, the current of the supporting solution.

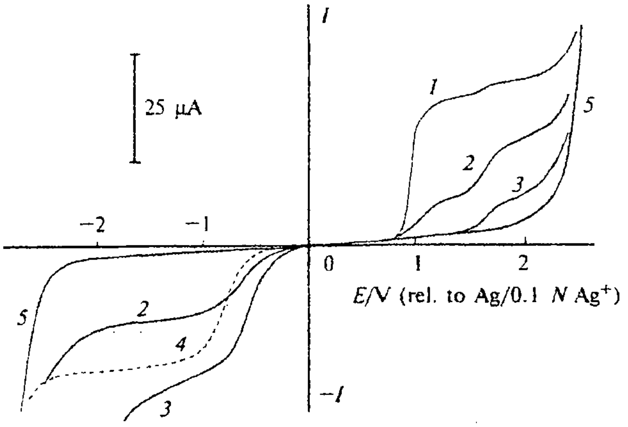


Fig. 3. Voltammograms recorded on a rotating disk Pt electrode: *1*, *2*, and *3*, the voltammograms recorded before, in the course of, and after microelectrolysis, respectively, of the tetrabutylammonium salt of MNAF (C = 3.9 · 10^{-3} mol L^{-1}) on a stationary Pt electrode (S = 2 cm) in a 0.1 N Bu_4NClO_4 solution in anhydrous MeCN at the potential E = 1.2 V; *4*, the voltammogram of MNAF (C = 3 · 10^{-3} mol L^{-1}); *5*, the current of the supporting solution.

corresponds to a one-electron transfer. Analogous behavior is observed for the 3-methoxy-4-nitraminofurazan (MNAF) anion, in which both substituents at the amine nitrogen atom possess acceptor properties. There are also two waves with $E_{1/2}$ = 0.9 and 1.7 V on the polarization curve of oxidation of this anion (see Fig. 3, curve *1*), the wave with $E_{1/2}$ = 1.7 V being poorly seen, like those on the polarization curves of oxidation of the other nitramine anions under study.

From the coulometric measurements it follows that the radical intermediates were formed at the first stage of oxidation of the nitramine anions under consideration:

$$R\bar{N}NO_2 - e \longrightarrow R\dot{N}NO_2\,.$$

It can be suggested that these species, like *gem*-dinitroalkyl radicals,[5] are unstable and one path of their stabilization involves the formation of NO_2 and the corresponding nitrene. In this case, the second and third waves on the polarization curves of the nitramines under consideration could correspond to oxidation of species that are directly formed upon fragmentation of radical intermediates or to oxidation of conversion products of these species. Previously, we observed this effect, in particular, the appearance of the wave of the nitrate ion, on the polarization curves of oxidation of gemdinitroalkane anions.[5] This suggestion is also seemingly supported by the fact that the waves appeared after the first waves on the polarization curve of oxidation of the initial nitramine anion were observed at the same potentials ($E_{1/2}$ =1.1 and 1.7 V) regardless of the structure of this anion.

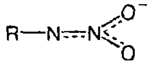
In the hope of obtaining additional data on the regularities of electrooxidation of nitramine anions, we performed a series of controlled potential microelectrolyses using voltammetric control over these processes. It appeared that 0.9 F per mole of the anion was required for completion of oxidation of the IPNA anion at the potential of 1.5 V. The first wave on the polarization curve, which was recorded in the course of electrolysis (see Fig. 1), gradually decreased (and disappeared at the end of electrolysis), while the wave with $E_{1/2}$ = 1.7 V noticeably increased and persisted on the polarization curve (see curve *1''*) after complete electrolysis. The latter wave coincides in potential with the oxidation wave of the nitrate anion (*cf.* curves *1''* and *4* in Fig. 1). In the course of electrolysis, the wave of the nonionized form of the IPNA anion with $E_{1/2}$ = −1.5 V appeared in the cathodic region and then increased (curves *1'* and *1''*). The amount of this form is 74% with respect to the theoretically possible value. This can be clearly seen from a comparison of the height of the cathodic wave that appeared after exhaustive oxidation of the IPNA anion (see Fig. 1, curve *1''*) with that of the nonionized IPNA species (curve *3*) taken for comparison at a concentration equal to that of the IPNA anion before microelectrolysis. Previously, we demonstrated[1] that electroreduction of primary nitramines on a Pt electrode in MeCN was accompanied by their deprotonation. Taking into account this fact, the solution obtained after oxidative electrolysis was subjected to exhaustive reductive electrolysis at the potential E = −1.8 V. This resulted in regeneration of the anion (see Fig. 1, curve *2*) in 70% yield, and the wave in the cathodic region (curve *1''*) disappeared.

From the aforesaid it follows that the radical intermediate, which is formed in the first stage of oxidation of the IPNA anion, is stabilized primarily due to abstraction of the H atom from the components of the medium and only partially undergoes other conversions to form, apparently, the NO_3^- anion as one of the final products.

Consumption of 0.84 F per mole of the anion was required for oxidation of the MNAF anion at the potential of 1.4 V. In this case, as in the case of the IPNA anion, the wave with $E_{1/2}$ = 1.7 V on the polarization curves, which were recorded in the course of electrolysis, increased and remained at the end of electrolysis (see Fig. 3). Simultaneously, the cathodic wave with $E_{1/2}$ = −0.65 V appeared and then increased. At the potentials of this wave, reduction of the nonionized form of MNAF ($E_{1/2}$ = −0.75 V; see. Fig. 3, curve *4*) is most likely accompanied by reduction of at least one more product with a less negative value of $E_{1/2}$.

Electrooxidation of the MNA and ENA anions exhibits distinguishing features. Thus, in both cases only 0.6—0.65 F per mole of the initial anion was required for complete microelectrolysis of these anions at potentials corresponding to the plateau of the second wave (E = 1.2 V), while 0.9 F per mole was required in the case of the IPNA anion (see above). Apparently, this is indicative of a nonelectrochemical way of consumption of the MNA and ENA anions. The anodic wave of the NO_3^- ion, which appeared on the polarization curves of solutions after oxidative electrolysis of the abovementioned anions, is substantially higher than that obtained after electrolysis of the IPNA anion (*cf.* curves *1''* in Figs. 2 and 1). Judging from the shape of the cathodic wave that appeared in the course of electrolysis, in both cases the nonionized forms of the nitramines were formed along with other readily reducible products (see Fig. 2, curve *1''*). This is consistent with the results of reductive electrolysis of the final solutions, which, according to the voltammetric estimation, led to regeneration of ≤30% of the initial MNA and ENA anions (this amount is substantially smaller than that in the case of the IPNA anion (70%, see above)) and, in addition, to the appearance of the oxidation wave ($E_{1/2}$ = −0.1 V) of new products (see Fig. 2, curve *2*).

Previously,[1] we mentioned that the reactivity of nitramine anions was determined by their ambident properties, which were manifested in the ability of these species to react both as N- and O-centered anions. Note that (according to the published data[6]) the O-centered anions predominante in solution. Hence, it can be assumed that electrooxidation of alkylnitramine anions also afforded O-centered anions.



Apparently, the involvement of the N atoms in partially or totally double bonds prevents fragmentation to form nitrene species. Attempts to detect nitrene in the course of oxidative electrolysis of the MNA, ENA, and IPNA anions using cycloaddition to cyclohexene or insertion into the C—H bond of dioxane (*cf.* the published data[7]) were unsuccessful. After electrolysis, an azo compound, which is a probable product of dimerization of nitrene or N-centered radical species (if they formed), were not detected in the reaction mixture.

It is more probable that in the first stage of oxidation of the MNA and ENA anions, the corresponding radicals are generated, while the transfer of the second electron to form cationic species occurs at potentials of the second oxidation waves of the above-mentioned anions. Apparently, subsequent conversions of these cations involve reactions with the initial anion, which sharply decrease the quantity of electricity consumed (0.6 F instead of 2 F per mole of anion for an at least two-electron process). Electrolysis afforded products which we failed to identify and was, apparently, accompanied by liberation of noticeable amounts of NO_2 molecules, which were converted into nitrate ions[8]

$$2\,NO_2 \longrightarrow NO^+ + NO_3^-.$$

The above-described conversions are to a substantially lesser extent characteristic of the IPNA anion. The major pathway of its oxidation involves the abstraction of the H atom from the components of the medium by the radical intermediate. Apparently, this is the reason for the absence of the wave with $E_{1/2}$ = 1.1 V on the polarization curve of oxidation of the IPNA anion. At the same time, the presence of the small oxidation wave of the nitrate ion on the polarization curve at the end of electrolysis (see Fig. 1, curve *1''*) indicates that the abstraction of the H atom from the components of the medium by the radical intermediate is not the only reaction pathway.

Unlike the MNA, ENA, and IPNA anions, the MNAF anion contains an acceptor substituent rather than a donor substituent at the amine N atom, which leads to redistribution of the electron density in the anionic structure. We believe that in this case, the probability of formation of the N-centered radical increases, which, in turn, should be reflected in the regularities of electrooxidation of the MNAF anion.

Actually, when 1 F of electricity per mole of the initial compound was passed through the reaction mixture, oxidation of the MNAF anion (E = 1.2 V) afforded 3,3-dimethoxyazofurazan (DMAF) in 21% yield. The voltammograms of DMAF recorded under standard conditions and given in Fig. 4 show that this compound is difficultly oxidized. The oxidation wave with $E_{1/2}$ = 1.84 V is extended and is obviously irreversible. To the contrary, the reduction wave of the DMAF anion with $E_{1/2}$ = −0.70 V is reversible (see Fig. 4) and, according to the data of coulometric measurements, corresponds to the attachment of one electron to form a stable radical anion. Noteworthy are the similar values of $E_{1/2}$ for the reduction waves of the MNAF and DMAF anions (−0.75 and −0.70 V, respectively; see Fig. 4, curves *1* and *4*). Hence it follows that the cathodic wave that appeared in the course of oxidative electrolysis of the MNAF anion (see Fig. 3, curve *3*) is at least a combination of reduction waves of the above-mentioned two compounds.

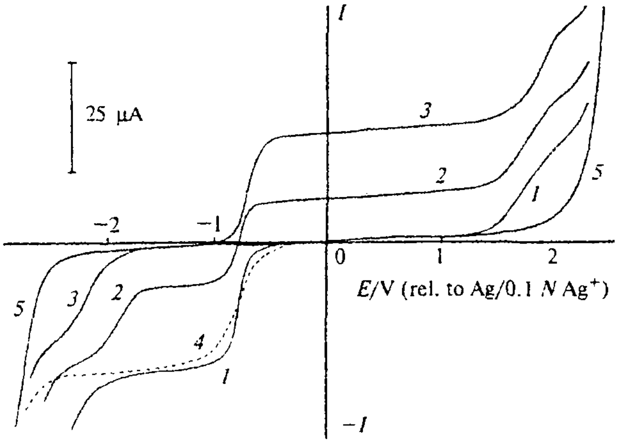
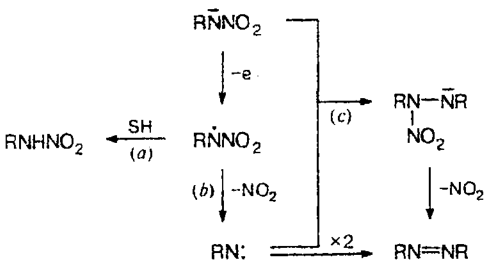


Fig. 4. Voltammograms recorded on a rotating disk Pt electrode: *1*, *2*, and *3*, the voltammograms recorded before, in the course of, and after microelectrolysis, respectively, of the tetrabutylammonium salt of DMAF (C = 3.1 · 10^{-3} mol L^{-1}) on a stationary Pt electrode (S = 2 cm) in a 0.1 N Bu_4NClO_4 solution in anhydrous MeCN at the potential E = −1.4 V; *4*, the voltammogram of MNAF (C = 3 · 10^{-3} mol L^{-1}); *5*, the current of the supporting solution.

Taking into account the data of voltammetric measurements and controlled potential electrolysis, the regularities of electrooxidation of the MNAF anion can be described by the following scheme:

Scheme 1



According to this scheme, the abstraction of the H atom from the medium is one of the probable ways of stabilization of the intermediate radical. Based on the voltammetric data and taking into account that the cathodic branch in curve *3* (see Fig. 3) corresponds to reduction of the multicomponent system, the contribution of process *a* is difficult to estimate precisely. Only the qualitative conclusion can be drawn that this contribution is substantially smaller than that in the case of oxidation of the IPNA anion.

Apparently, fragmentation of the radical (*b*) to form nitrene followed by dimerization affords an azo derivative and competes with abstraction of the H atom. This compound can be also formed in the reaction of nitrene with the initial anion. However, note that route *b* is accompanied by liberation of nitrogen dioxide, while route *c* leads to generation of the nitrite ion.

From this standpoint, route *b* seems to be preferential. Actually, 1 F of electricity per mole of the initial anion is required both in the case of route *b* and that of route *c*, which agrees with the experimental data (0.84 F per mole, see above). However, route *c* is associated with generation of the nitrite ion, whose oxidation wave ($E_{1/2}$ = 0.2—0.3 V) is absent on the polarization curves recorded in the course of oxidative electrolysis of the MNAF anion. Note that Scheme 1 reflects only the most probable conversions of the MNAF anion but does not give an exhaustive account of conversions. This is evident, for example, from the fact that oxidation of the MNAF anion (judging from the value of $E_{1/2}$ for the cathodic wave that appeared on the polarization curve; see Fig. 3, curve *3*) afforded (along with MNAF and DMAF) an unknown readily reducible product.

Therefore, the regularities of electrooxidation of the nitramine anions are to a large extent determined by their structures. Nitrene species would be expected to be formed in electrooxidation of nitramine anions containing an acceptor substituent at the amine N atom.

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References

1. V. A. Petrosyan, V. A. Frolovskii, and D. A. Sadilenko, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 83 [*Russ. Chem. Bull.*, 1999, **48**, 82 (Engl. Transl.)].
2. V. Masaki and M. Ohta, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 1808.
3. L. Herzog, M. Gold, and R. Geckler, *J. Am. Chem. Soc.*, 1951, **73**, 749.
4. A. V. Fokin, I. V. Tselinskii, S. F. Mel'nikova, S. N. Vergizov, Yu. N. Studnev, V. P. Stolyarov, and S. S. Il'in, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2086 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1901 (Engl. Transl.)].
5. V. A. Petrosyan, M. E. Niyazymbetov, A. G. Bazanov, I. V. Tselinskii, and A. A. Fainzil'berg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2726 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29**, 1901 (Engl. Transl.)].
6. Yu. V. Serov, A. G. Bazanov, and I. V. Tselinskii, *Zh. Org. Khim.*, 1980, **16**, 472 [*J. Org. Chem. USSR*, 1980, **16** (Engl. Transl.)].
7. T. Fuchigami and T. Nonaka, *Denki Kagaku*, 1985, **53**, 582.
8. A. Boughriet, A. Coumare, J. C. Fischer, and M. Wartel, *J. Electroanal. Chem.*, 1986, **200**, 217.

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