

# Strategy for Controlling the Kolbe Electrosynthesis in the Presence of Aromatic Fragments and Amino Groups in the Molecule

N. V. Smirnova, E. G. Neganova\*, E. A. Astaf'ev\*, O. A. Petrii\*, G. A. Tsirlina\*,  
and I. P. Beletskaya\*

*Southern Russia State Technical University, Russia*

*\* Moscow State University, Vorob'evy gory, Moscow, 119899 Russia*

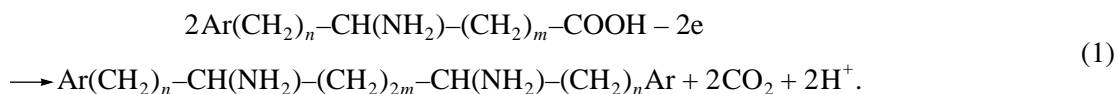
Received August 31, 2000

**Abstract**—A general characteristic of processes that occur during anodic oxidation of phenylacetic and phenylpropionic acids and derivatives of  $\alpha$ - and  $\beta$ -amino acids on platinum electrodes in methanol and mixed pyridine–methanol solutions is given. From preparative electrolyses in stagnant and flow-through reactors, conditions are determined under which the dimerization (Kolbe electrosynthesis) is least complicated by the formation of polymer products. Properties of removed electrodes, on which stable polymer films formed during the electrosynthesis, are examined. For films formed in certain conditions on the cathode, the presence of a quasi-reversible redox transition is demonstrated. Such films contain disperse platinum codeposited with polymer as a result of the anode dissolution in the cells with common compartments. In principle, the film-modified electrodes can be used for controlling anodic decarboxylation.

## INTRODUCTION

The electrochemical oxidation of carboxylates, called the Kolbe reaction, is one of the earliest reactions in the organic chemistry. As a result of 150 years of studies, it has found numerous synthesis applications [1–3]. At the same time, extending this method of dimerization of organic molecules to a wide range of functionally substituted carboxylic acids, extremely promising for the synthesis of complexones and other chelating ligands and chiral bases is hampered by many factors, which include the concurrent oxidation of substituents, formation of polymer products, and dissolu-

tion of the anode metal. Some success achieved in the last few years in this direction for organophosphorus compounds [4] points to the feasibility of satisfactory yields of symmetric dimers. Therefore, it seems worthwhile to estimate the possibilities of optimization of the Kolbe synthesis for, at the very least, another important group of reactants, specifically,  $\alpha$ - and  $\beta$ -amino acids, which contain an aromatic ring, and formulate the possibilities and limitations of electrosynthesis of corresponding 1,2- and 1,4-diamines via reactions of the type



The alternatives for the synthesis of these important products include performing catalytic reactions in rather severe conditions (see, for example, [5]) and fail to ensure high yields.

During anodic oxidation of  $\alpha$ -amino acids in conditions typical for the Kolbe synthesis (smooth platinum electrodes in methanol, current density of about  $0.1 \text{ A cm}^{-2}$ ), the dimerization occurs with low and even zero yields and the predominant reaction is that of anodic methoxylation [6]. Concurrently, there occur processes that are accompanied by the reagent destruction, even processes that lead to the formation of polymer products. It is worth noting that both these compli-

cations are also typical for aromatic carboxylic acids that contain no amino groups, say, for phenylacetic acid [7, 8].

It was found empirically that a dimer yield can be increased by introducing considerable amounts of pyridine (Py) into the methanol solutions [2, 9]. The mechanism of the action of pyridine and similar additives is not quite clear yet. It was only assumed that, in principle, organic additives can undergo oxidation with the formation of active species, interact with intermediate radicals or carbonium ions, and significantly redistribute the content of components in the reaction layer.

We have undertaken a study of some modeling processes, which involve  $\alpha$ - and  $\beta$ -substituted carboxylic acids, in the framework of an effort to synthesize bisphosphines, diamines, and bisphosphonates with the aid of the Kolbe reaction. The aim of this project is to supplement the known preparative results by information on the kinetics of the processes and the specific structure of interfaces. Up to now, detailed polarization measurements in the conditions of the Kolbe reaction [10] and studies of the forming adsorbates [11, 12] were performed largely for aliphatic nonsubstituted reactants. The related problem of the nature of polymer films and the place the possible electropolymerization processes occupy in the overall kinetic scheme of anodic processes have not been discussed in the literature. At the same time, as demonstrated in an elegant study [13], the surface of a carbon electrode can be modified in the course of anodic oxidation of aryl acetates.

We also have undertaken an attempt to raise the dimer yield and overcome complications associated with the polymerization by using a flow-through reactor instead of a stagnant one. The design of flow-through reactors, which are extensively used in synthesis studies [14], is usually oriented on the forced removal of gaseous products from the reaction zone, which lowers the gas content in the solution, thus diminishing considerable ohmic losses caused by the gas. To our minds, in a flow-through reactor, the thick films of polymer products are removed from the electrode surface by the solution flow, as is the case with the anodic oxidation of terminal amines [3]. That is why one of the specially undertaken aims was constructing a flow-through reactor of an optimal design.

## EXPERIMENTAL

The experiments on the Kolbe electrosynthesis were carried out in reactors of two types. In a stagnant three-electrode cooled reactor with common compartments, the working and auxiliary electrodes were plates of smooth platinum with a visible area of 1 cm<sup>2</sup>, arranged in parallel about 1 mm apart. The reference electrode was an aqueous silver–silver chloride electrode, to which all the potentials  $E$  are referred below. It was positioned in a proper place through a bridge with two stopcocks underneath the solution level in the working compartment in order to prevent the penetration of chloride ions.

The flow-through reactor of Teflon was a flow-through reaction chamber with two parallel nickel cathodes and a platinum anode positioned in between. The electrode areas could be varied in the interval 1–10 cm<sup>2</sup> by selecting a proper screening Teflon gasket with through holes. The gap between the anode and cathodes was 1 mm. The solution was continuously supplied into the chamber with the aid of an electric pump from an external tank at a rate reaching 0.5 l min<sup>-1</sup>. When constructing the flow-through reactor, all its parameters

were selected on the basis of preliminary experiments. In the experiments, maximum thicknesses of films formed during the time period required for the reactant to undergo complete conversion were estimated.

The polarization was imposed in the course of syntheses and electrochemical measurements from P-5827 and PI-50-1 potentiostats. The current and potential responses were recorded with an  $x$ - $y$  recorder.

The solvent was dehydrated methanol purified by boiling and distillation over magnesium methylate [15] and containing 20 vol % Py. The pyridine was purified by distillation over sodium. Commercial phenylacetic acid (bp 120°C at 1.75 kPa, mp 77 to 78°C) and phenylpropionic acid (bp 145–147°C at 3.15 kPa, mp 48°C) were distilled and then neutralized with a 1 M sodium methylate solution in methanol. 2-Amine-3-phenylpropionic acid (Merk) and 3-amine-3-phenylpropionic acid (synthesized by the technique, described in "Synthesis of Organic Preparations," vol. 3, p. 61) were acylated by adding acetic anhydride and a 4 M NaOH solution while cooling with ice. Once the reaction terminated, we added concentrated hydrochloric acid (to adjust pH to about 3) and isolated the precipitates of 2-acetylamino-3-phenylpropionic acid (mp 149°C) and 3-acetylamino-3-phenylpropionic acid (mp 161°C) (150°C [16] and 161 to 162°C [17], respectively).

After performing the preparative electrolysis, acetic acid was added into reaction mixtures (until neutralization), the solid products were filtered off, and the solvent was removed from the filtrate on a rotor. The extracts from the oils thus produced were obtained using chloroform, ether, and acetone. The non-Kolbe product, (1-methoxy-2-phenyl)ethylamide of acetic acid, was identified by its mp (100.5°C; according to [18], 99.5°C). To identify this substance and 1,4-diphenyl-1,4-diacetylaminoethane (mp 235°C), we relied upon PMR spectroscopy (Varian VXR-400, working frequency 400 MHz). The amount of nonreacted source reactants and 1,2-diphenylethane and 1,4-diphenylbutane was determined by the gas–liquid chromatography (GLC) method (Tsvet 500 chromatograph, mode  $T_{\text{det}} = T_{\text{exp}} = 250^\circ\text{C}$ ,  $T_{\text{col}} = 60\text{--}170^\circ\text{C}$ , 5°C per min). Dimers with bp of 110–115°C and 155–160°C (at 0.35 kPa), when isolated, were pure by GLC (according to the literature data, bp of 284°C [19] and 317°C [20], respectively). The yields presented in this work are averaged over two to five experimental runs.

After a preparative electrolysis, the electrodes were removed from the cell, rinsed with twice-distilled water, and placed in three-electrode cell with separated compartments filled with a 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution prepared from twice-distilled water and sulfuric acid twice-distilled in a vacuum. In these experiments, the reference electrode was a reversible hydrogen electrode in the same solution (RHE). Examination of the removed electrodes with the aim of detailing the state of their surfaces in the course of a Kolbe electrosynthesis, which was carried out earlier in [6, 7], revealed the

phenomenon of adsorption of organic compounds at high anodic potentials. However, for studying films on electrodes, such a technique as applied to the problem of the Kolbe synthesis is exploited for the first time.

## RESULTS AND DISCUSSION

### General Characteristic

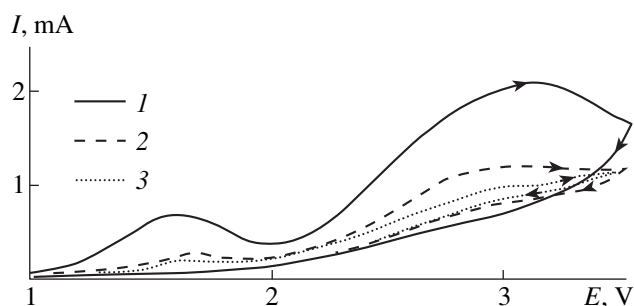
The processes that occur in the systems under study at high anodic potentials are severely non-steady-state; therefore, it is impossible to determine such formally kinetic parameters as Tafel slopes and exchange currents for fixed portions of polarization curves (PC) when compared with the data for other processes in [14]. The pseudosteady-state curves measured in phenylacetic acid solutions (the current is recorded 10–20 min after passing to the next potential value) reveal two Tafel portions with slopes of 250–300 mV separated by a portion with a higher slope of about 1 V in the interval  $2.0 < E < 2.2$  V.

The main feature of non-steady-state PC is the presence of a shallow peak in the potential region  $1.0 < E < 1.7$  V (Fig. 1). The more positive the potential corresponding to the beginning of a sweep and the longer the exposure time at it, the lower the peak. The peak is always absent in the reverse run of the curves. The peak steadily diminishes in successive measurements in each anodic run of PC. Simultaneously, the current in the portion of smooth growth at  $E > 1.7$  V decreases as well. No such phenomenon was observed in supporting electrolytes, at least at similar acidity of the media. Therefore, it seems natural to refer it to the process of chemisorption of the reactant. The increase in the current at higher potential can be attributed to the occurrence of faradaic processes, including those involving the solvent. Raising the anodic limit of the studied interval of potentials to 3.5 V allows us to observe a decrease in the current at  $E > 3$  V, which is especially strongly pronounced in the first cycle (curve 1).

Introducing 20 vol % Py into methanol solutions makes the current decrease throughout the entire range under study by two to three times. The non-steady-state peak current remains intact, though. Increasing the degree of neutralization of the acid by sodium methy-late leads to a systematic shift of PC in the direction of lower potentials. On the whole, all the basic features of PC qualitatively conform to those known for aliphatic carboxylic acids [10].

### Preparative Electrolysis

The preparative electrolysis was run for 10–40 h at 2.2–2.4 V (Ag/AgCl) and in galvanostatic modes at 30–300 mA cm<sup>-2</sup>. In the former case, the current would decrease by an order of magnitude within the first 10–20 min. In the latter case, the potential rapidly increased to values exceeding five to six volts. This points to high ohmic losses. Simultaneously, we observed with the

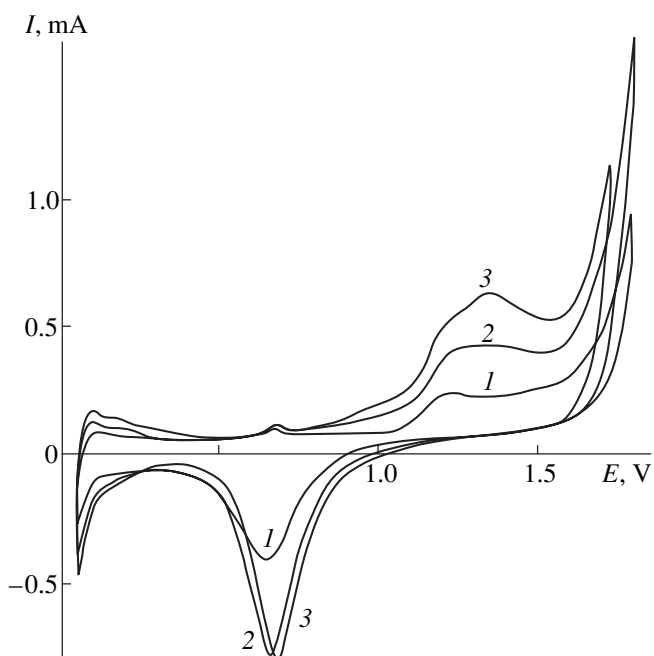


**Fig. 1.** Voltammetric curves for Pt electrode in a methanol solution of 1 M phenylacetic acid and 0.5 M sodium methalate;  $v = 2$  V min<sup>-1</sup>; curve numbers correspond to cycle numbers; prior to measuring curve 1, electrode was polarized at 0.5 V for 5 min.

unaided eye the growth of the films and the coloring of solution into yellow (sometimes, brown) hue. The latter was, at least to some degree, probably connected with the formation of some soluble complexes of platinum, because the state of the anodes after terminating the electrolysis apparently testified to the occurrence of corrosion processes.

When oxidizing phenylacetic and phenylpropionic acids in pyridine-free methanol solutions, a complete conversion of the source reactants occurred upon passing a charge exceeding the theoretical values by 50–70%; the yield of formed dimers (1,2-diphenylethane and 1,4-diphenylbutane, respectively) did not exceed 10–12%. The dimer yields in a stagnant reactor reached 30–40% (calculated per reacted substance) after adding 20 vol % Py; however, no complete conversion occurred even after a charge in excess of two to three times the theoretical value was passed. It was impossible to run the reactions for longer times in both galvanostatic and potentiostatic modes because of the formation of polymer films on the anode and especially the cathode (below, we call such films anodic and cathodic). In stagnant electrolyte in the cell with common compartments, the films' thickness reached a few hundred micrometers and sometimes caused short-circuiting, which unequivocally points to a conducting character of the films. All this forced us to specially investigate properties of polymers that form during Kolbe syntheses (see below).

In the flow-through reactor, the dimer yields in the presence of pyridine reach 60–70% at the same degrees of conversion of phenylacetic and phenylpropionic acids (50–70%). The films on the electrodes are much thinner than in the stagnant reactor, but the polymer continuous to grow throughout the entire experiment duration; eventually, the solid product peels off the surface and accumulates in the external tank. A longer electrolysis and, correspondingly, a more complete conversion, is hampered by a gradual increase in the hydrodynamic resistance, which may be associated with both an increase in viscosity and the formation of



**Fig. 2.** Voltammograms for smooth Pt electrode covered with anodic film, recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $\nu = 2 \text{ V min}^{-1}$ ; curve numbers correspond to cycle numbers.

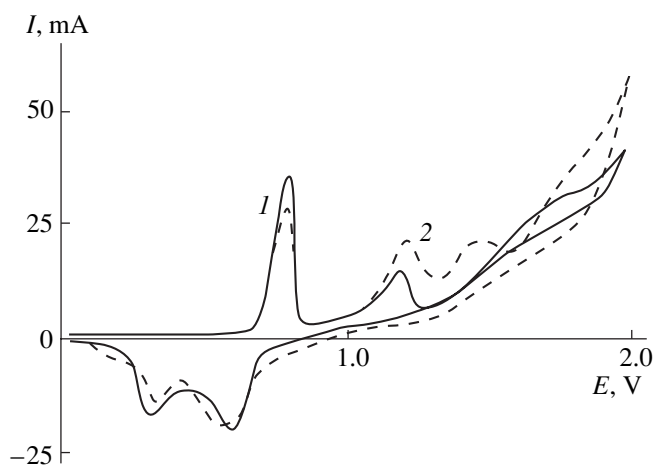
a polymer suspension. This new hindrance, as opposed to those discussed in the foregoing, is not of fundamental importance and can be overcome by improving the design of the reactor chamber and the pump.

For amino acids under study, the efficiency of introducing pyridine is much lower. For 2-amine-3-phenylpropionic acid, the dimer yields did not exceed the detection limit, but the yield of (1-methoxy-2-phenyl)ethylamide of acetic acid was 64%. In the case of 2-amine-3-phenylpropionic acid, the dimer yield did not exceed 8–10%. Frankly speaking, both preliminary results can be of some synthetic interest, because we have discovered no alternatives for the synthesis of 1,4-diamines of this particular composition in the literature.

In the future, it would make sense to extend the technique based on use of a flow-through reactor to the amine-substituted reactants. However, it is necessary to first solve the problem of an increase in the conversion degree, because the source reactants are more expensive and because much larger amounts of solution would be required.

#### *Properties of Polymer Products*

After passing a charge that did not exceed 1 to 2% of the theoretical value (as calculated per dimer formation), the anodic film thickness remained almost unchanged. Conversely, the cathodic film continued to grow in the stagnant reactor during the entire experiment, until it filled the interelectrode spacing. Simultaneously, a fraction of the polymer peeled off and settled



**Fig. 3.** Voltammograms for smooth Pt electrode covered with cathodic film, recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $\nu = 2 \text{ V min}^{-1}$ : (1) first and (2) tenth cycles.

on the reactor bottom. In cyclic voltammograms (CVA) for the electrode modified with anodic film (Fig. 2) we see that the double-layer region of potentials extends as compared with that common for platinum electrodes in the same solution; the hydrogen adsorption is substantially suppressed, although not completely; and the CVA progress considerably alters in the oxygen adsorption region. In the course of a potentiodynamic treatment, the film undergoes desorption (curves 2, 3), and the curve gradually becomes analogous to those characteristic of pure platinum. The desorption occurs probably during both anodic and cathodic polarization.

On the whole, we conclude that the anodic film has pores the solution can penetrate and is prone to irreversible redox processes accompanied by desorption. The fact of the formation of a film (and not of a submonolayer of the adsorbate) should be taken into account when considering the mechanism of anodic processes in the systems under study.

Of much more interest, to our minds, is the behavior of cathodic films on the removed electrode. The films are very thick and sometimes happen to be more stable during a potentiodynamic polarization in an aqueous acid solution even if the potential of the anodic polarization limit exceeds 1.5 to 2.0 V (RHE) (Fig. 3). Thick cathodic films heavily affect the oxygen adsorption and evolution and completely suppress the hydrogen adsorption. The reversible redox processes that occur in the films at potentials of about 0.7 V (RHE) manifest themselves by a sharp anodic and forked cathodic current peaks in the voltammograms (Fig. 4). To a first approximation, the heights of the peaks are proportional to the potential scan rate  $\nu$ . The splitting of the cathodic peak may be attributed to the superposition of the peak of desorption of adsorbed oxygen atoms; however, this question calls for further research.

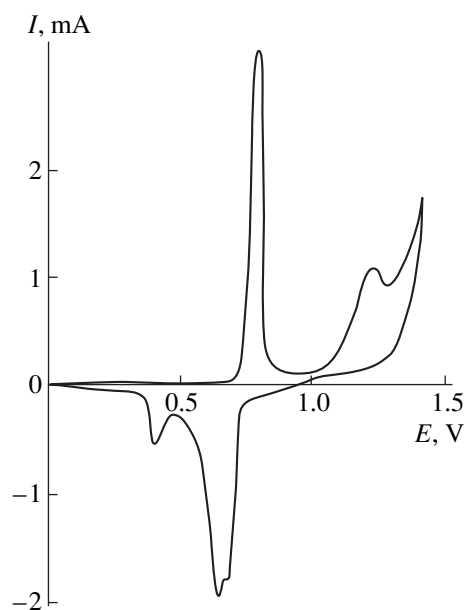
The estimated values of the charge spent for the oxygen adsorption at the electrode and for redox conversions in the film unambiguously suggest that the film is rather thick (dozens of effective monolayers undergo charge-discharge) and contains platinum microparticles. The latter probably form during cathodic reduction of platinum complexes, i.e. products of the anode dissolution. The developed surface of deposited platinum provides roughness factors reaching 100; nevertheless, no hydrogen adsorption on platinum was observed.

The reversible redox conversions observed when cycling potential are typical for a class of conducting polymers under active investigation [21]. On platinum and some other electrodes, such polymers form during anodic polymerization of organic molecules, which is a complicated process connected with intermediate formation of radicals. In the system under discussion, the formation of such a film was fixed during a cathodic process. It is not improbable that the polymerization process occurring during a Kolbe synthesis in pyridine-containing solutions is analogous to the formation of films on a mercury cathode in aqueous acid solutions observed in [22]. Unfortunately, the redox behavior of the film on mercury was not studied in [22]. Nonetheless we conclude, on the basis of the data published in [22], that the film obtained by the authors had dielectric properties and reduced the electrode capacitance almost to zero.

The attempt to produce a similar cathodic film in pyridine-containing methanol solutions in the absence of organic acids has gone awry, probably due to indeterminate conditions of the cathode polarization in a poorly conducting pyridine-methanol environment. It is quite probable though that the film formation results from co-polymerization of pyridine and phenyl acetate (propionate) or products of their electrochemical conversions. In principle, we cannot rule out polymerization of platinum complexes with organic ligands either.

Specifics of the polarization mode in which redox-active films form also warrants further research. We have managed to produce them exclusively in galvanostatic modes, while gradually decreasing potential. In simple potentiostatic modes, a cathodic polarization leads to the formation of visually identical but mechanically less strong films whose outer part is readily removed when transferred into an aqueous sulfuric acid solution. The thin semitransparent film left on the electrode is also resistant to polarization but displays no pronounced redox transitions. However, from the magnitude of the charge in the hydrogen region, one can clearly fix the presence of dispersed platinum in it, and the roughness factors reach 100.

The fact that the cathodic film remains stable during anodic polarization makes it possible to use electrodes modified with it as anodes in the Kolbe electrosyntheses. It is not improbable that this might give a promising way for controlling anodic decarboxylation, which



**Fig. 4.** Typical voltammogram for smooth Pt electrode covered with cathodic film, recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $v = 2 \text{ V min}^{-1}$ .

would not require introducing additives into solution when performing preparative electrolyses.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 99-03-33 487a.

#### REFERENCES

- Schäfer, H.J., *Comprehensive Organic Synthesis: Selectivity, Strategy, and Efficiency in Modern Organic Chemistry*, Trost, B.M. and Fleming, I., Eds., Oxford: Pergamon, 1991, vol. 3, p. 633.
- Ebersson, L., in *Organic Electrochemistry: An Introduction and a Guide*, Baizer, Ed., New York: Marcel Dekker, 1973.
- Weiper-Idelmann, A., Kahmen, M., Schäfer, H.J., and Gockeln, M., *Acta Chem. Scand.*, 1998, vol. 52, p. 672.
- Sugiya, M. and Nohira, H., *Bull. Chem. Soc. Jpn.*, 2000, vol. 73, p. 705; *Chem. Lett.*, 1998, p. 479.
- Volckaerts, E., Geise, H.J., Daelemans, F., and Claereboudt, H., *Bull. Soc. Chim. Belg.*, 1992, vol. 101, p. 497.
- Linstead, R.P., Shephard, B.R., and Weedon, B.C.L., *J. Chem. Soc.*, 1951, p. 2854.
- Linstead, R.P., Shephard, B.R., and Weedon, B.C.L., *J. Chem. Soc.*, 1952, p. 3624.
- Coleman, J.P., Lines, R., Utley, J.H.P., and Weedon, B.C.L., *J. Chem. Soc., Perkin Trans. 2*, 1974, p. 1064.
- Ross, S.D. and Finkelstein, M., *J. Org. Chem.*, 1969, vol. 34, p. 2923.
- Vijh, A.K. and Conway, B.E., *Chem. Rev.*, 1967, vol. 67, p. 623.

11. Fioshin, M.Ya. and Mirkind, L.A., *Itogi Nauki Tekh., Ser.: Elektrokhimiya*, 1972, vol. 8, p. 273.
12. Mirkind, L.A. and Tyurin, Yu.M., *Elektrosintez i mekhanizm organicheskikh reaktsii* (Electrosynthesis and Mechanism of Organic Reactions), Moscow: Nauka, 1973, p. 181.
13. Andrieux, C.P., Gonzalez, F., and Saveant, J.-M., *J. Am. Chem. Soc.*, 1997, vol. 119, p. 4292.
14. Yan, J.-F., Fedkiw, P.S., and Law, C.G., *J. Appl. Electrochem.*, 1996, vol. 26, p. 175.
15. Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
16. *Beilstein Handbook of Organic Chemistry*, Berlin: Springer, 1988, vol. 14, suppl. II, p. 302.
17. *Beilstein Handbook of Organic Chemistry*, Berlin: Springer, 1988, vol. 14, suppl. II, p. 493.
18. Lokensgard, J., Fisher, J., and Bartz, W., *J. Org. Chem.*, 1985, vol. 50, pp. 26, 5609.
19. *Beilstein Handbook of Organic Chemistry*, Berlin: Springer, 1982, vol. 5, p. 598.
20. *Beilstein Handbook of Organic Chemistry*, Berlin: Springer, 1982, vol. 5, p. 616.
21. *Electroactive Polymer Electrochemistry*, Lyons, M.E.G., Ed., New York: Plenum, 1994, part 1; 1996, part 2.
22. Fedorova, A.I. and Vasina, S.Ya, *Elektrokhimiya*, 1967, vol. 3, p. 742.