SIXTH ALL-UNION CONFERENCE ON POLAROGRAPHY

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From November 17-19, 1975, the Scientific Council on Analytical Chemistry of the Academy of Sciences of the USSR, the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR, and the Latvian Branch of the D. I. Mendeleev All-Union Chemical Society conducted the Sixth All-Union Conference on Polarography in Riga.

The principal attention of the conference was focused on the following timely problems.

1. New instrumental methods of investigation and devices in polarography and voltamperometry in microelectrodes, and automation of experiments by means of computers.

2. The study of the mechanism and kinetics of organic electrochemical processes, and the use of polarography for the solution of problems in organic chemistry.

3. The application of voltamperometric methods in biochemistry and pharmacology (for the study of physiologically active compounds, biopolymers and their transformations, and monitoring of environmental pollution).

4. The polarography of complexes of metals and the application of complexing substances in polarography.

A distinctive feature of the conference was predominance of the problems involved in the polarography of organic compounds.

More than 300 specialists, including representatives of 140 scientific institutes from 60 cities of the USSR and prominent specialists of the German Democratic Republic, Poland, Hungary, Czechoslovakia, and Yugoslavia, participated in the proceedings of the conference. In order to achieve more efficient organization of the conference, the principal material from 240 concrete private communications was set forth in 27 review and review-report papers, and, in addition, 22 private communications were presented.

Papers by S. G. Mairanovskii (Moscow) on the development of theoretical concepts in the polarography of organic compounds and by Ya. P. Stradyn' (Riga) on the role of polarography in the modern complex of research on organic compounds were presented in the first plenary session.

Three thematic sessions were devoted to an examination of the mechanism and kinetics of organic electrochemical processes and to diverse possibilities of polarographic and voltamperometric methods in the study of biologically active substances and in biochemistry and pharmacology.

The constantly increasing interest in solid microelectrodes, on which processes involving electrical oxidation of organic compounds can be studied, was reflected in papers by Yu. V. Pleskov and L. N. Nekrasov.

In the closing plenary session, Academician of the Academy of Sciences of the Moldavian SSR Yu. S. Lyalikov, L. M. Madan, and Yu. D. Sister (Kishinev) related the application of new modifications of the polarographic method in the analysis of organic compounds. The newest data on the application of nonaqueous solvents in polarography were set forth in a comprehensive paper by S. I. Zhdanov (Moscow). Professor Yu. P. Kitaev (Kazan) demonstrated new possibilities for the joint use of polarography and physical methods such as photoelectronic spectroscopy and chemical polarization of nuclei in the study of the reactivities of

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organic compounds. The principles of the electrochemistry of heterocycles with two nitrogen atoms in the 1,4 position (pyrazine, quinoxaline, phenazine, and pyrazine and phenoxazine N-oxides) were presented in a paper by I. Folke (Prague, Czechoslovakian SSR).

The conference demonstrated interest in the utilization of polarography in scientific research and monitoring of industrial processes, including the application of polarography in organic chemistry, particularly in the chemistry of heterocycles (in recent years papers of polarographic character in our journal constituted ∿2.5% of the total number of published papers).

A large amount of new data on the electrochemical conversion and study of the reactivities of heterocyclic systems was presented at the conference. O. M. Polumbrik and N. G. Vasil'kevich (Kiev) established the order of reductive and oxidative activities of stable organic radicals, including heterocyclic radicals, from polarographic half-wave potentials. Interest was aroused by the data of A. V. Lizogub, A. F. Pozharskii, and T. I. Vinokurova (Leningrad, Rostov-on-Don) on the polarographic behavior of peri-condensed heteroaromatic cations. Thus, a study of the polarographic behavior of these ions showed that they are more electrophilic than benzimidazolium ions having the same amidine system of bonds in the heteroring. The mechanism of the reduction of perimidinium salts also differs from the mechanism of the reduction of substituted benzimidazolium salts and proceeds in two one-electron diffusion steps; this indicates the higher stability of the resulting free radicals as compared with radicals of the benz- and naphthoimidazole series. By comparing the $E_{1/2}$ values of the first wave of heteroaromatic cations one can conclude that perimidinium ions are intermediate between quinolines and benzimidazolium ions with respect to electrophilicity.

I. Ya. Kravis, Ya. T. Stradyn', and L. É. Neilande (Riga) determined the Hammett constants of indanedionyl and 4- and 5-azaindanedionyl groupings by means of polarography, and V. P. Kadysh, Yu. É. Fridmanis, and É. S. Lavrinovich (Riga) studied the electrochemical reduction of isomeric 2-pyridiniaindane-1,3-diones — dipolar compounds having two electrochemically active fragments (pyridinium and indanedione). V. T. Glezer and P. V. Zikmanis (Riga) succeeded in synthesizing and studying the electrical reduction of fixed azonium cations with the azonium nitrogen atom of a purine ring; these cations are of interest as model substances for the study of the mechanism of the reduction of organic azo compounds. The trend of the electrical reduction of unsubstituted benzoyl-, alkyl-, and arylsulfohydrazones of N-alkylquinolones, benzothiazolinones, and indolinones, which was found to be valuable for the prediction of the activities of these compounds in the creation of new materials for color photography, was elucidated in a paper by G. P. Sennikov, S. I. Zhdanov, and co-authors (Moscow). L. M. Baider and co-workers (Riga) studied the development of free radicals during the electrical reduction of oximes of aldehydes and glyoxals of the 5-nitrofuran series, demonstrating that secondary radicals are formed in the case of glyoxal oximes as a result of Beckmann rearrangement.

M. G. Polievktov and co-workers (Moscow) presented data on the mechanism of the reduction of substituted 5-phenylfurfurals and 5-nitrophenylfurans and, in another of their communications, refined the mechanism of the electrical reduction of coumarin. Yu. I. Beilis and co-authors (Khar'kov, Donetsk, and Kherson) studied the anode oxidation of derivatives of benz- and naphthimidazoles. I. Ya. Putninya and V. Ya. Vegnere (Riga) made a detailed study of the polarographic reduction and complexing of arylazothiazoles. The distinctive character of the mechanism of the polarographic reduction of 6-pyridazone derivatives when electron-acceptor substituents are introduced was discovered by V. T. Glezer, Ya. P. Stradyn', and co-authors (Riga). Whereas only the C=C bond of the pyridazone ring is usually involved in electrical reduction, the introduction of electron-acceptor substituents also gives rise to cleavage of the heteroring N–N bond. Yu. M. Kargin and co-authors (Kazan') studied the electrochemical reactivities of N-substituted maleinimides, thereby explaining some of the observed anomalies of the lactim–lactam rearrangement of maleinimide in dimethylformamide. V. Sh. Tsveniashvili (Tbilisi) showed the role of self-protonation in the reduction of hydroxy derivatives of benzo-2,1,3-thiadiazole, which is realized through dissociation of the OH group rather than through the formation of an intramolecular hydrogen bond, as previously assumed. New data on the oscillopolarography of 6-mercaptopurine and 2- and 4-thiouracils, which are basically of analytical interest, were compiled in a communication by E. D. Arkhangel'skaya and V. I. Gorokhovskaya (Kazan). The anode oxidation of 8-mercaptoquinoline was studied by I. M. Bessarabov and O. A. Songin (Alma-Ata), and the oxidation of 3,5-

dicarbonyl-1,4-dihydropyridines was studied by Yu. I. Beilis, G. Ya. Dubur, and co-authors (Khar'kov, Riga). Several communications by Moscow scientists were devoted to the voltamperometric study of iminoxyl radicals and their conversion products.

The peculiarities of the polarographic reduction of 1,2-dihydroquinazolin-2-ones and their seven-, eight-, and nine-membered analogs were elucidated by A. V. Bogat-skii and co-authors (Odessa).

N. P. Shimanskaya and co-workers (Khar'kov), on the basis of polarographic data, showed that the half-wave potentials and the mechanism of the reduction change both in the case of 4-aryloxazolyl- or 4-aryloxadiazolyl-substituted derivatives of naphthalic anhydride and in the case of 2,5-diphenyloxazole derivatives containing a 1,2-diarylethylene group in the meta position of the 2-phenyl ring because of the mutual effect of the unconjugated oxazole and vinyl groupings. M. M. Evstifeev and co-authors (Rostov-on-Don) established that the mechanism of the electrode process in the electrochemical reduction of salts of the benzopyrylium series consists in reversible transfer of one electron to give free radicals, which undergo dimerization; the effect of the structure of the salt on the peak potential and the stability of the radicals formed in the process was demonstrated. V. A. Serazetdinova and B. V. Suvorov (Alma-Ata) detected an interesting effect of ammonium ions on the polarographic behavior of some alkylcyanopyridines — the addition of NH_4^+ ions has the same effect as in increase in the concentration of hydrogen ions, i.e., the ammonium ions act as proton donors with respect to the pyridine ring.

A very large amount of material on the application of polarography for the study of physiologically active compounds was presented. For example, the combination of voltamperometry with thin-layer chromatography and mass spectrometry enabled A. V. Bogat-skii and co-authors (Odessa) to detect 1,2-dihydro-3H-1,4-benzodiazepines and their transformation products in blood plasma, the brain, the liver, and the microsomal fraction of the liver of experimental animals. Interesting data were obtained by E. F. Kalistratova and co-workers (Irkutsk) and A. B. Dmitrieva and co-workers (Pyatigorsk) on the polarographic behavior of flavone and flavonoids. E. S. Kosmatyi and co-workers (Kiev) presented data on the application of polarography and oscillopolarography for the determination and study of the transformations of extremely diverse pesticides in the environment. I. K. Tutane, Ya. V. Ogle, and Ya. P. Stradyn' (Riga), together with co-workers of the Institute of Physical Chemistry of the Polish Academy of Sciences, developed a method for the chromatopolarographic separation of mixtures of 5-nitrofuran derivatives (furadonine, solafur, furacilin, and their potential biotransformation products).

One should especially note the research of Academician I. Ya. Postovskii and co-workers (Sverdlovsk, Tula), in which it is demonstrated that the aza effect and the annealation effect during nucleophilic substitution in heteroaromatic compounds can be evaluated from the reduction potentials on a dropping-mercury electrode.

If one also takes into account several communications presented at the conference in which the reactivities of heterocyclic compounds are estimated from their capacity for complexing with inorganic ligands, it can be stated that all aspects of the application of polarographic and voltamperometric methods for the elucidation of the mechanisms of the transformations and the quantitative evaluation of the reactivities of various heterocyclic systems were represented at the Riga conference. The seventh conference is scheduled to be organized in Tbilisi in 1978.