POLAROGRAPHY IN INITIAL STAGES OF ELUCIDATION OF ORGANIC ELECTRODE PROCESSES

Petr ZUMAN

Department of Chemistry, Clarkson University, Potsdam, NY 13699-5810, USA;
e-mail: zumanp@clarkson.edu

Received September 10, 2009
Accepted December 29, 2009

Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of the 50th anniversary of the Nobel Prize for polarography.

To develop a reliable electroanalytical method, it is essential to understand – at least in principle – the nature of physical and chemical processes involved. DC polarography is a useful tool in initial stages of elucidation of processes involving reductions and oxidations of organic compounds in aqueous solutions. Main information to be obtained involves: the number of reduction and oxidation steps, the number of electrons transferred in each step, the nature of the transport of electroactive species, the roles of fast, slower and slow chemical reactions (such as proton transfers or hydration–dehydration equilibria), in particular those preceding electron transfer and the structure of the electrolysis product. The used tools are: (i) Measurements of the limiting current and half-wave potentials and their dependence on composition of the supporting electrolyte; (ii) dependences on drop-time and scan-rate; (iii) product identification; (iv) comparison with structurally related compounds, experimentally and from literature. Examples of reductions of the following bonds are given. Single bonds: C–X (X = halides, OR, OH, NH_2, SR), N–Y (Y = O, N, S), O–O, N–N, S–S. Double bonds: C=C, C=N, C=S, N=N, and also triple bonds: C≡C, C≡N. Examples of oxidations are those of phenols and of enediols. Anodic waves due to mercury salt formations are observed for thiols, urea and thiourea derivatives (barbiturates, thiobarbiturates), and dithiocarbamates. References are restricted to our work.

Keywords: Electroreduction; Electrooxidation; Polarography; Mechanisms of elucidation; Electroactive groups.

In application of any analytical method, it should be understood – at least in principle – what physical and chemical processes are involved. Only under such conditions an analytical method can be used effectively. The establishment of the nature of physical and chemical processes involved is straightforward in many analytical methods. In electroanalytical methods,

Collect. Czech. Chem. Commun. 2009, Vol. 74, Nos. 11–12, pp. 1757–1776

doi:10.1135/cccc2009122

the situation is often more complex and an extensive information about the role of the supporting electrolyte on the shape of recorded current–voltage curves may be needed. Majority of electroanalytical methods is carried out in aqueous solutions, hence the following discussion will be restricted to such solutions. To obtain reliable current–voltage curves, it is sometimes necessary to use also solutions containing either strong acids or strong bases. Nevertheless, the use of buffered solutions and pH between 2 and 12 is strongly recommended.

First information sought is the range of pH, in which the investigated compound is either reduced or oxidized. To obtain this information, it proved useful to make first a general test. For this purpose are used solutions of a 0.1 M strong acid, like hydrochloric, perchloric or sulfuric, acetate buffer pH 4.7, phosphate buffer pH 6.8, borate buffer pH 9.3, and 0.1 M solution of sodium hydroxide. Current–voltage curves are recorded in 0.1 mM solutions of the investigated compounds in the above acids, bases or buffers. Only if in some acidity range the investigated compound, even at relatively low concentrations, is not sufficiently soluble, an organic solvent is added to increase the solubility. It is preferable if the concentration of the organic solvent could be kept below 30% v/v. At these concentrations the presence of the organic solvent usually does not affect strongly pH of the buffer used. As a co-solvent acetonitrile is preferred. It increases the solubility and has a relatively small effect on pH.

The use of dimethyl sulfoxide or dimethylformamide is sometimes possible, but these solvents limit the use of spectrophotometric methods, which are often useful for comparison with the behavior obtained by electroanalysis. The ethanol can be used as a co-solvent only under condition that the alcohol or, in alkaline solutions, alcoholate, does not interact with the investigated compound.

Once the rough pH range of the supporting electrolyte, in which the investigated species is electroactive, is found, a more detailed investigation is carried out over the pH range, in which the investigated compound is reduced or oxidized. Current–voltage curves are usually recorded in 0.3–0.4 pH unit intervals. In this approach the use of simple buffers, rather then "universal buffers" is recommended.

The role of proton transfers is then found based on the changes of limiting currents and half-wave potentials with pH. A decrease in the limiting current with increasing pH for the reductions indicates that in more acid media the electron transfer is preceded by or interposed between electron-transfers. A decrease of the anodic oxidation wave with decreasing pH indicates that the electroactive species is a conjugate base. When the half-wave potentials are shifted with pH, this indicates that one or more proton transfers are involved in the electroreduction or electrooxidation. If the half-wave potential is pH-independent in the whole pH range, no proton transfer is involved in the electroreduction or -oxidation. If the half-wave potential becomes pH-independent only over a certain range of pH, no proton transfer plays a role in this pH range.

The next step is the proof of the number of electrons transferred in the electrode process, that yields a limiting current. The simplest way to obtain an information about the number of transferred electrons, is to compare (in the chosen pH range) the behavior of the investigated compound with that of organic compounds of a related structure or comparable size, for which the number of transferred electrons is known.

Whenever it is possible, the information about the number of transferred electrons (which often indicates the nature of the electrolysis product) is compared with an identification of the structure of such product obtained by controlled potential electrolysis. The most informative is carrying out the controlled potential electrolysis with the same electrode as used for recording of current–voltage curves. Preparative electrolyses with a dropping mercury electrode must be carried out in a small volume, e.g. 0.5 ml, otherwise they would take a too long time. Even in a small volume, preparative electrolysis must be carried out usually over a period of 8–10 h. This has the disadvantage that during this time-period, the product can undergo consecutive chemical reactions.

Very often the controlled potential electrolysis is carried out with a mercury pool electrode in a larger volume of 5–7 ml. The surface of such electrodes should be renewed by stirring using a magnetic stirrer. With this type of electrolyses and somewhat higher concentration of the investigated compound, e.g. 1.0 mmo l^{-1}, the electrolyses can be carried out within 1–3 h. The limitation of this approach is that the processes at a large surface electrode may be different from that on the dropping mercury electrode. If the limiting current is dependent on pH, it is often useful to obtain information about the nature of the limiting current. When a limiting current decreases with increasing pH to about 15% of the initial value, it is recommended to follow the dependence of the limiting current on the mercury pressure or drop-time. If the current is diffusion controlled, it is a linear function of concentration of the electroactive species and the limiting current is dependent on square root of the mercury column height. When the drop-time is controlled, the dependence of the current on drop-time will follow a parabola corresponding to $i = \text{const}\cdot t^{1/6}$ (Fig. 1).

If the current is independent of mercury pressure or if its changes with drop-time follow a parabola, that corresponds to $i = \text{const}\cdot t^{2/3}$, it is an indication that the current is limited by the rate of a chemical reaction, which takes place in the vicinity of the electrode (kinetic current) (Fig. 2). Such currents are also a linear function of concentration of the investigated species. If the current is a non-linear function of concentration, some adsorption phenomena are involved very often.

Concerning the instrumentation used in polarographic studies, it should be mentioned that the modern digital instruments, using a mercury drop

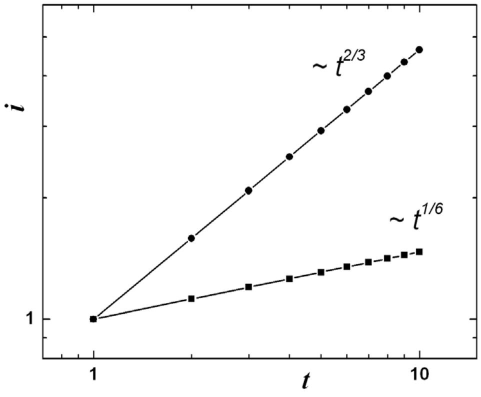


FIG. 1
Dependence of logarithm of current during the life of a single drop on time

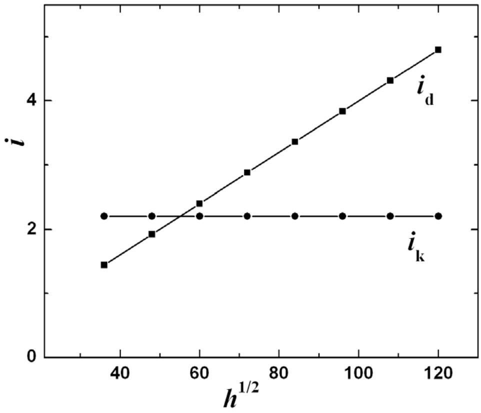


FIG. 2
Dependence of diffusion current i_d and kinetic current i_k on the height h of mercury reservoir

electrode with a mechanically controlled drop-time, are well suited for analytical applications. For fundamental research are preferred analog instruments in connection with a naturally growing dropping mercury electrode. All available theoretical treatments were namely developed for such dropping electrode, with a surface area reaching a limiting value with time. When mechanical drop-control is used, the electrode surface is terminated, before the limiting surface area is reached. Moreover, the majority of the available treatments offer information for mean recorded current rather than for peak current, that is sometimes recommended. The peak current is namely more sensitive to the presence of traces of surface active compounds.

Another variable, which should be followed, is the dependence of limiting currents on time after the studied compound was added to the reaction mixture. Such changes indicate chemical reactions which take place in the bulk of the solution. It is useful to compare the time changes of such limiting currents with those in UV-Vis spectra. In some instances and with some instruments NMR can also offer information about the kinetics of the bulk reaction. Nevertheless, in the majority of cases and for most NMR spectrometers used the concentration at which NMR can be followed is considerably higher than that used in polarography or UV-Vis spectrophotometry. The identification of the electrolysis product is a time consuming process. In some instances it is possible to obtain some information about the reduction or oxidation of the investigated type of compound from the literature. Thus, in the Handbook Series of Organic Electrochemistry[1], it is possible to find information not only about the currents and potentials at which the compound is oxidized or reduced, but also about in many cases about the number of electrons transferred in the process and in some instances also the structure of the product. Information about the mechanisms of numerous electroprocesses can be found in review articles[2]. The largest collection of information about reduction or oxidation of organic compounds can be found in the treatises[3] authored first by Baizer and Lund and later by other collaborators. Nevertheless, these volumes bring information predominantly about the preparative electrolyses and the resulting products, less about the sequence of transfer of electrons and protons. Valuable information can be also obtained from the encyclopedia by Bard and Lund[4].

Reductions and oxidations of numerous types of chemical bonds in organic compounds will be briefly discussed.

REDUCTIONS OF HALOGEN-CONTAINING ORGANIC COMPOUNDS

The two-electron process, resulting in formation of a halide anion, is initiated by a transfer of a single electron. The reduction of the radical formed in this process takes place at more positive potentials than the transfer of the first electron and, therefore, only a two-electron reduction is observed[5–10] [(*1*) and (*2*)].

$$\mathrm{>CR{-}X + e \;\rightarrow\; >CR^{\bullet} + X^{-}} \qquad (\mathrm{X^{-}} = \text{halide}) \tag{1}$$

$$\mathrm{>CR^{\bullet} + e + H^{+} \;\rightarrow\; >CHR} \tag{2}$$

The potentials of reduction become more positive in the sequence: fluorine, chlorine and bromine derivatives and, at most positive potentials, those of iodine. The reduction is facilitated by substitution on both the carbon, to which the halogen is bound, and on adjacent carbons.

Thus the potential of reduction invariably increases with increasing number of halogen atoms bound to a single carbon, for instance in the sequence: monochloro, dichloro, and trichloro compounds[11]. Reductions are also facilitated by a grouping adjacent to the carbon–halogen bond, e.g. by a carbonyl or a carboxyl group.

It should be kept in mind, that the activating group should not be reduced at more positive potentials than the carbon–halogen bond. So, e.g., the easily reducible nitro group adjacent to a halogen is reduced first and, therefore, does not directly influence the reduction of the carbon–halogen bond. It should be remembered that the reducibility of the carbon–halogen bond is affected predominantly by the inductive effect of the adjacent groups. If the halocarbon group is located on an aromatic ring, the reduction of the carbon–halogen bond will be affected by substituents in *ortho*, *meta*, and *para* positions. The effects of subtituents in *meta* and *para* positions can be expressed by linear free energy relationships. The situation with the substituents in *ortho* position is more complex as, in addition to the inductive effects, direct field effects and substituent size play a role.

CLEAVAGE OF C–N, C–O, AND C–S BONDS

The reductive cleavage of other single bonds is more complex. The cleavage of the C–N [12–14], C–O [15–17], and C–S [15–17] bonds usually takes place only if they are activated. This can be achieved either by an adjacent group in a chain or by a subsituent on benzene or another aromatic ring. Thus the reduction of C–O, C–N or C–S single bonds can take place in an aliphatic compound or in the straight-chain part of a molecule, provided that a carbonyl group is present adjacent to the carbon of the carbon–nitrogen or carbon–oxygen bond [(*3*) and (*4*)]. Such bonds can be also cleaved, when a $CH_2\text{-}OH_2^+$, $CH_2\text{-}NH_2$ or $CH_2\text{-SR}$ group is present in position 4 of a pyridine ring[18].

$$\mathrm{PhCOCH_2Y + 2\ e + 2\ H^+ \rightarrow PhCOCH_3 + HY} \qquad (3)$$

where Y = OH, OR, NHR, SH, SR, SR_2^+

$$\mathrm{PhCOCH_3 + 2\ e + 2\ H^+ \rightarrow PhCH(OH)CH_3} \qquad (4)$$

The activating group in the reduction of a C–N bond can also be a cyano group in the $CH(NH_2)\text{-}C{\equiv}N$ grouping[19].

REDUCTIONS OF N–O, N–N, O–O, AND S–S SINGLE BONDS

Types of compounds, where a four-electron reduction, is initiated by a two-electron transfer and cleavage of the N–O or N–N bonds occurs, are those of oximes[20–28] [(*5*)–(*7*)], hydrazones[29–33] [(*8*) and (*9*)], followed by (*7*) and probably also semicabazones[34]. To undergo such reductions, oximes or hydrazones must be diprotonated. Proton transfers take place by fast reactions in the vicinity of the electrode. For hydrazones, such reactions take place in homogeneous solutions. For oximes, the heterogeneous protonations take place on oxime adsorbed at the electrode surface.

$$\mathrm{>C{=}NOH + 2\ H^+ \rightarrow >C{=}NH_2^+OH_2^+} \qquad (5)$$

$$\mathrm{>C{=}NH_2^+OH_2^+ + 2\ e \rightarrow >C{=}NH + H_2O} \qquad (6)$$

$$\mathrm{>C{=}NH + 2\ e + 2\ H^+ \rightarrow >CHNH_3^+} \qquad (7)$$

$$\mathrm{>CH{=}NNH_2 + 2\ H^+ \rightarrow >CHNH^+NH_3^+} \qquad (8)$$

$$\mathrm{>CHNH^+NH_3^+ + 2\ e \rightarrow >CH{=}NH + H_2O} \qquad (9)$$

As the imines formed in the two-electron cleavage of N–O bonds in oximes or N–N bonds in hydrazones are reduced at more positive potentials than the N–O or N–N bonds, any imine formed by electrolysis is immediately further reduced and a four-electron wave results.

The single bonds in peroxides (*10*) and disulfides (*11*) can be also electrochemically reduced. Whereas the reduction of the peroxides and hydroperoxides is an irreversible process, the reduction of the disulfide bonds is complicated by the possibility of the reaction of the resulting sulfide radicals or anions with the metallic mercury of the electrode.

$$\mathrm{R{-}O{-}O{-}R' + 2\ e + 2\ H^+ \ \rightarrow\ 2\ ROH} \tag{10}$$

$$\mathrm{R{-}S{-}S{-}R' + 2\ e + 2\ H^+ \ \rightarrow\ 2\ RSH} \tag{11}$$

HYDROGENATION OF C=C BONDS

The reduction of isolated C=C bonds takes place at too negative potentials to be followed in aqueous solutions. With increasing number of conjugated C=C bonds, the reduction potentials are gradually shifted to more positive values.

When the C=C group is activated by an adjacent carbonyl group in α-, β-unsaturated aldehydes and ketones, hydrogenation of the C=C group takes place[35–40] in most cases [(*12*) and (*13*)].

$$\mathrm{PhCOCH{=}CHR' + 2\ e + 2\ H^+ \ \rightarrow\ PhCOCH_2CH_2R'} \tag{12}$$

$$\mathrm{PhCOCH_2CH_2R + 2\ e + 2\ H^+ \ \rightarrow\ PhCH(OH)CH_2CH_2R'} \tag{13}$$

REDUCTION OF C=N, C=O, AND C=S BONDS

In C=N, C=O, and C=S groupings, the bond between the carbon and the heteroatom is hydrogenated. The reduction is facilitated in the sequence from nitrogen to sulfur derivatives. In the reduction of carbonyl compounds[41–43], the protonated form is sometimes reduced in acidic media in two one-electron waves. Because the first wave corresponds to the reduction of the protonated form, its half-wave potential is shifted to more negative values with increasing pH [(*14*)–(*16*)]. The half-wave potential of the reduction of the radical, which occurs in the second one-electron process, is pH-independent. As a result the two one-electron steps gradually merge with sufficiently increased pH into a single two-electron step.

$$>C{=}O + H^+ \rightarrow >C{=}OH^+ \quad (14)$$

$$>C{=}OH^+ + e \rightarrow [>C{-}OH]^{\bullet} \quad (15)$$

At high pH values, usually above pH 10, the one two-electron wave splits again into two one-electron processes. In this pH range it is the unprotonated form of the carbonyl compound, that is reduced by accepting one electron [(*16*) and (*17*)]. The radical anion is then reduced at more negative potentials. As the radical anion can be again protonated or reacts with cations of the supporting electrolyte, the more negative wave can be shifted to even more negative potentials. This results in the separation of the two one-electron waves.

$$>C{=}O + e \rightarrow [>C{=}O]^{\bullet -} \quad (16)$$

$$[>C{=}O]^{\bullet -} + e + 2\,H^+ \rightarrow CHOH \quad (17)$$

Such type of processes can be observed for reduction of benzaldehydes[44,45], acetophenones[46–52], and benzophenone[53] related compounds. Not all carbonyl compounds are reducible in the whole pH range to allow investigation of the overall mechanism described above. Reductions of aliphatic aldehydes[54–60], pyridinecarboxaldehydes[61–64] and some other heterocyclic aldehydes, and that of ketones α-substituted with halogens, particularly fluorine, are considerably affected by hydration–dehydration equilibria.

The reduction of some alicyclic ketones[65–67] of 1,2-dicarbonyl compounds[67–70] (*18*) and α-keto acids (*19*) and their esters[71–73] has also been reported.

$$>COCO< + 2\,e + 2\,H^+ \rightarrow CH(OH)CO \quad (18)$$

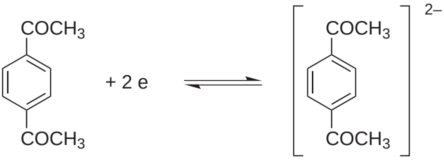
$$>COCOOR + 2\,e + 2\,H^+ \rightarrow CH(OH)COOR \quad (19)$$

It is mostly conjugation that facilitates their reduction. Nevertheless, both half-wave potentials and limiting currents are also affected by hydration–dehydration [(*20*) and (*21*)] and keto–enol equilibria, as well as in alkaline solutions, the formation of carbanion-enolates (*22*). The formation of such anions affects also reduction of 1,3-dicarbonyl compounds[74–77].

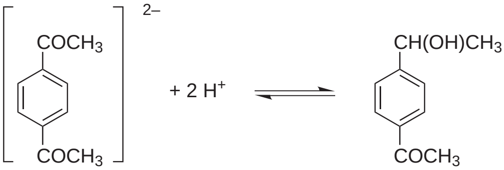
$$\mathrm{RCOCOOR' + H_2O \rightarrow RC(OH)_2COOR'} \qquad (20)$$

$$\mathrm{RCOCOOR' + OH^- \rightarrow RC(OH)(O^-)COOR} \qquad (21)$$

The shifts of half-wave potentials of benzaldehydes, due to substituents in 3- or 4-position, can be expressed by the modified Hammett equation[78–81]. When the substituent is another carbonyl grouping, the reduction may be accompanied by antecedent or consecutive chemical reactions. Thus, the diprotonated form of 1,4-diacetylbenzene undergoes in acidic media a two-electron reversible reduction[82] (*22*). The product of this electrochemical process is only slowly converted into (4-hydroxyethyl)benzaldehyde (*23*). This type of reduction has been observed for other 1,4-dicarbonylbenzenes[83], including terephthalaldehyde.

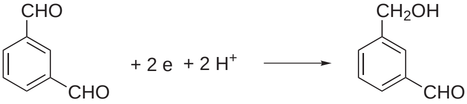


(*22*)



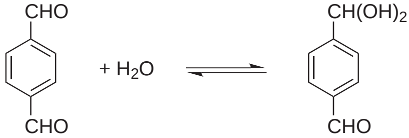
(*23*)

Recently, attention has been paid to the behavior of the three isomeric benzenedicarboxaldehydes using polarography, as well as UV-Vis and NMR spectra[84–93]. Most straightforward is the reduction of the benzene-1,3-dicarboxaldehyde, the isophthalaldehyde[84–86,90] (*24*), where the effect of the second formyl group on the reduction of the first one can be described by the Hammett substituent constant. Polarographic *i*–*E* curves of this isomer thus resemble those of an equimolar mixture of 3-cyano- and (3-hydroxyethyl)benzaldehyde (the effect of the cyano group resembles that of the formyl group).

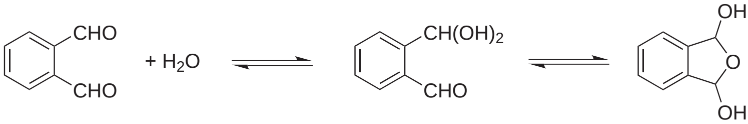


(*24*)

Whereas the majority of benzaldehydes is hydrated in aqueous solutions in less than 3% [94], polarographic curves[85,88,90] proved that the strong resonance interaction of the two formyl groups in positions 1 and 4 results in a 15% hydration of one CH=O group in terephthalaldehyde (*25*). Even a more complex behavior was observed[85,87,89,90,92,93] for the 1,2-isomer, orthophthalaldehyde (*26*). This compound is widely used in determinations of amino acids and for cleaning of surgical instruments. Polarography together with UV-Vis and NMR spectra demonstrated that this dialdehyde is present in aqueous solutions in three forms. Only about 18% of the orthophthalaldehyde remains unhydrated, about 8% is present as an acyclic monohydrate and about 74% as a cyclic hemiacetal. The behavior of recently proposed naphthalene-2,3-dicarboxaldehyde[84] is similar, but this dialdehyde is less hydrated.



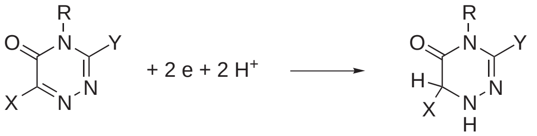
(*25*)



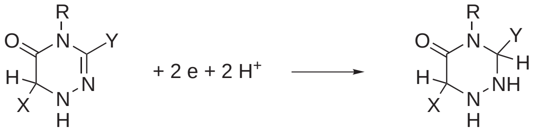
(*26*)

Imines, under the condition, where they are sufficiently stable and do not undergo hydrolysis, are reduced in a two-electron reduction to an amine[29,92,93,95–97] (*7*). These conditions are usually fulfilled for imines derived from aromatic aldehydes and ketones and for those derived from aldehydes and ketones at pH > 8 in the presence of an excess of the amine. Reduction of imines as intermediates in reductions of oximes and hydrazones was discussed above.

In heterocyclic compounds containing C=N double bonds, this bond often undergoes a two-electron reduction. The reduction takes place in protonated forms of the heterocycle. The reductions of azomethine (C=N) bonds take place in pyrimidines, pyrazines, and 1,2,4-triazines[98–112] [(*27*) and (*28*)]. In most of these compounds used as pesticides, protonated ($C=NH^+$-) forms undergo reductions. In pyridazines, which bear two C=N bonds in locations N(1)=C(6) and N(2)=C(3), the 1,6-C=N bond is reduced at potentials by several hundred millivolts more positive than the reduction of the 2,3-C=N bond.



(*27*)



(*28*)

Even more informative is the role of substituents on C_6 and C_1. Whereas the effects of substituents at C_6 on the reduction of the N(1)=C(6) bond followed the trend predicted by linear free energy relationships, the potential after introduction of a substituent on C_3 practically remains unchanged. This indicates lack of conjugation through the N(1)–N(2) bond. Thus whereas the N=C-C=N group is conjugated, the C=N-N=C system is not. The latter grouping thus contains a single N–N bond, as confirmed by the bond length obtained from crystalographic data. The available information about the reduction of the C=S double bond is relatively limited.

REDUCTION OF NITROSO AND NITRO COMPOUNDS

Reduction of the double bond in nitroso compounds has not been investigated in much detail. The available information deals with reduction of substituted nitroso benzenes[113–115].

$$\mathrm{PhNO} + 2\ \mathrm{e} + 2\ \mathrm{H}^+ \quad \rightarrow \quad \mathrm{PhNHOH} \qquad (29)$$

On the other hand, a very substantial amount of information is available about the reduction of nitro compounds[116–128]. This reduction usually takes place in a four-electron step yielding an arylhydroxylamine [(*30*)–(*32*)]. This product is reduced in acid media in a two-electron irreversible wave at more negative potentials than that of the nitro group [(*33*) and (*34*)].

$$\mathrm{PhNO_2} + \mathrm{e} \quad \rightarrow \quad [\mathrm{PhNO_2}]^{\bullet-} \qquad (30)$$

$$[PhNO_2]^{\bullet -} + H^+ \rightarrow PhNO_2H^{\bullet} \qquad (31)$$

$$PhNO_2H^{\bullet} + 3\ e + 3\ H^+ \rightarrow PhNHOH + H_2O \qquad (32)$$

$$PhNHOH + H^+ \rightarrow [PhNHOH]H^+ \qquad (33)$$

$$[PhNHOH]H^+ + 2\ e + 2\ H^+ \rightarrow PhNH_2 + H_2O \qquad (34)$$

It has been proved[129] that in the four-electron process the first step is transfer of a single electron, which is reversible and which is followed by consecutive transfers of protons and three more electrons. The interpretation of the shift of $E_{1/2}$ with increasing pH to more negative potentials of the four-electron reduction wave of nitrobenzenes was proposed by Laviron[129]. The present author[118] erroneously assumed that the observed potential shifts can be attributed to a proton transfer taking place before the uptake of the first electron, as is the case for the majority of reductions of organic compounds in aqueous solutions.

Aliphatic nitro compounds are mostly reduced in a single four-electron step to the corresponding hydroxylamine. In aliphatic polynitro compounds the reduction in some instances results in the cleavage of the C–N single bond and production of the nitrite anion. In others, reduction of the nitro group yields a hydroxylamine derivative.

The substitution of the aromatic ring follows linear free energy relationships. This applies to substituents of nitrobenzene in positions 3 and 4 on the benzene ring and corresponding positions in polycyclic aromatic compounds. If a substituent, particularly a large one, is placed in position 2 or 6 of nitrobenzenes, a steric hindrance of coplanarity of the benzene ring and the nitro group appears. The removal of the nitro group from the plane of the aromatic ring results in a limited interaction of the nitro group with the benzene ring and a potential shift to more negative values occurs.

OTHER REDUCTIONS

Derivatives of acetylene (with a triple bond between carbon atoms) have been less thoroughly studied than corresponding C=C compounds. Compounds with a triple bond between carbon and nitrogen[130–133], bearing a cyano group, can undergo either reduction to a corresponding amide or lose a cyanide anion in the process of reduction. Among other compounds that contain nitrogen, most attention has been paid to azo compounds. Particularly the reduction of azo dyes has been more extensively studied. Diazo compounds and diazonium cations are also reducible[134,135]. Some attention has been paid to nonbenzenoid aromatic compounds, like tropylium ions[136,137], azulenes[138], and among heterocyclic species, to some anthocyanines[139] and sydnones[138,140–144].

OXIDATIONS

A high overvoltage of hydrogen on mercury allows to reach negative potentials (up to –2.5 V). As reductions of numerous organic compounds in aqueous solutions take place at potentials more negative than about –1.0 V, a large number of reductions of organic compounds has been reported[1]. The reductions are manifested by a cathodic wave. On the other hand, a number of organic compounds undergos oxidation at potentials more positive than +0.5 V. Mercury electrodes are nevertheless oxidized, yielding mercury ions, at +0.4 V or at more negative potentials. Hence, only the most easily (at potentials more negative than +0.4 V) oxidized organic compounds can be followed, using a dropping mercury electrode. In oxidation, on *i–E* curves, the current increases in the opposite direction to that for reduction and anodic waves are observed. Among organic compounds that undergo oxidations are hydroquinones, phenols[145–147], and enediols[148–152]. Oxidation of aldehydes[89,91,153–163] is observed in alkaline solutions where an addition of a hydroxide ion takes place [(*35*) and (*36*)]. This addition of the hydroxide ion occurs in a fast reaction in solution in the vicinity of the electrode surface. The product of this reaction is a geminal diol anion, which is oxidized to a carboxylic acid anion.

$$\mathrm{PhCHO + OH^- \;\rightarrow\; PhCH(OH)O^-} \tag{35}$$

$$\mathrm{PhCH(OH)O^- \;\rightarrow\; PhCOO^- + 2\,e + H_2O} \tag{36}$$

Anodic waves are also observed, when mercury ions (generated at the electrode surface by electrooxidation of metallic mercury) react with organic species present in solution. Such species can be molecules or ions, that form with mercury ions slightly soluble or complex products.

$$\mathrm{Hg \;\leftrightarrow\; Hg_2^{2+} + 2e} \tag{37}$$

$$Hg_2^{2+} + n\ X^- \quad \rightarrow \quad Hg_2(X_n)^{(n-2)} \qquad (38)$$

Often anodic waves of this type reach a limiting value with increasing concentration of the studied species. This can be attributed to the coverage of the surface by a monolayer of a slightly soluble compound. From the concentration corresponding to the monolayer formation and the determined electrode surface, it is possible to calculate the surface occupied by a molecule of the adsorbed, slightly soluble compound. In some compounds at concentrations higher than that, at which the first wave reached the limiting value, another anodic wave is observed at more positive potentials. This wave, at a sufficiently high concentration, also reaches a limiting value. Sometimes, even a third, more positive adsorption wave is observed.

There are several interpretations of the presence of several adsorption waves: change of the adsorbate structure from a flat placement of the molecules at the surface to that, where the molecule is adsorbed by an edge of a crystal, by one grouping or even one atom. Another possibility is a change in chemical composition of the adsorbate, e.g. in the oxidation state of mercury or a change in the ratio of mercury to the ligands involved. Finally, a change from a monolayer to a multilayer cannot be excluded. Attempts to identify the absorbate nature by isolation were unsuccessful as the isolated slightly soluble product underwent changes with time, indicating a role of solid-state reactions. Anodic waves due to formation of slightly soluble mercury compounds have been observed particularly for organic thiols[156,164–169], dithiols such as 2,3-dimercaptopropanol (BAL)[170–175], derivatives of urea[176–178] such as barbiturates and uracil, derivatives of thioureas[179–183] such as thiobarbiturates, and dithiocarbamates[184–188].

My gratitude is expressed to Mrs. R. Zuman for technical preparation of this manuscript during my incapacity to work and Doc. Dr. L. Pospíšil for careful editing and help.

REFERENCES

1. Meites L., Zuman P., et al.: *Handbook Series in Organic Electrochemistry*, Vols I and II, CRC Press, Cleveland 1977; Vol. III, CRC Press, W. Palm Beach 1978; Vol. IV, CRC Press, Boca Raton 1980; Vol. V, CRC Press, Boca Raton 1982; Vol. VI, CRC Press, Boca Raton 1983.
2. Zuman P.: *Adv. Anal. Chem. Instrum.* **1963**, *2*, 219.
3. a) Baizer M. M., Lund H. (Eds): *Organic Electrochemistry*, 2nd ed. M. Dekker, New York 1983; b) Lund H., Hammerich O. (Eds): *Organic Electrochemistry*, 4th ed. M. Dekker, New York 2001.

4. Bard A. J., Lund H. (Eds): *Encyclopedia of Electrochemistry of the Elements*, Org. Sect., Vols XI–XV. M. Dekker, New York 1973–1984.
5. Zuman P.: *Chem. Listy* **1962**, *56*, 21.
6. Romer M. M., Zuman P.: *J. Electroanal. Chem.* **1975**, *64*, 258.
7. Scott W. J., Zuman P.: *J. Chem. Soc., Faraday Trans.* **1976**, *72*, 1192.
8. Szafranski W. A., Zuman P.: *J. Electroanal. Chem.* **1975**, *64*, 255.
9. DeBoer H. S., Zuman P., van Oort W. J.: *Anal. Chim. Acta* **1980**, *120*, 31.
10. Scott W. J., Zuman P.: *Anal. Chim. Acta* **1981**, *126*, 71.
11. Scott W. J., Zuman P.: *Anal. Chim. Acta* **1981**, *126*, 259.
12. Horák V., Zuman P.: *Collect. Czech. Chem. Commun.* **1961**, *26*, 173.
13. Zuman P., Horák V.: *Collect. Czech. Chem. Commun.* **1961**, *26*, 176.
14. Ždanov S. I., Zuman P.: *Collect. Czech. Chem. Commun.* **1964**, *29*, 960.
15. Zuman P., Tang S.: *Collect. Czech. Chem. Commun.* **1963**, *28*, 829.
16. Manoušek O., Exner O., Zuman P.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 3988.
17. Fleury M. B., Tohier J., Zuman P.: *J. Electroanal. Chem.* **1983**, *143*, 253.
18. Manoušek O., Zuman P.: *Collect. Czech. Chem. Commun.* **1964**, *29*, 1432.
19. Zuman P., Manoušek O., Horák V.: *Collect. Czech. Chem. Commun.* **1964**, *29*, 2906.
20. Manoušek O., Zuman P.: *Experientia* **1964**, *20*, 30.
21. Zuman P., Exner O.: *Collect. Czech. Chem. Commun.* **1965**, *30*, 1832.
22. Kapetanovic V., Aleksic M., Zuman P.: *J. Electroanal. Chem.* **2001**, *507*, 263.
23. Baymak M. S., Celik H., Lund H., Zuman P.: *Tetrahedron Lett.* **2004**, *45*, 5113.
24. Aleksić M., Kapetanović V., Zuman P.: *Collect. Czech. Chem. Commun.* **2004**, *69*, 1429.
25. Celik H., Ekmekci G., Ludvík J., Pícha J., Zuman P.: *J. Phys. Chem. B* **2006**, *110*, 6785.
26. Celik H., Ludvík J., Zuman P.: *Electrochim. Acta* **2006**, *51*, 5845.
27. Celik H., Ludvík J., Zuman P.: *Electrochem. Commun.* **2006**, *8*, 1749.
28. Celik H., Ludvík J., Zuman P.: *Electrochim. Acta* **2007**, *52*, 1990.
29. Zuman P.: *Chem. Rev.* **2004**, *104*, 3217.
30. Baymak M. S., Lund H., Zuman P.: *Electrochem. Soc. Proc.* **2004**, *2004–2010*, 169.
31. Baymak M. S., Celik H., Lund H., Zuman P.: *J. Electroanal. Chem.* **2005**, *581*, 284.
32. Baymak M. S., Celik H., Lund H., Zuman P.: *J. Electroanal. Chem.* **2006**, *589*, 7.
33. Baymak M. S., Zuman P.: *Tetrahedron Lett.* **2006**, *47*, 7991.
34. Fleet B., Zuman P.: *Collect. Czech. Chem. Commun.* **1967**, *32*, 2066.
35. Barnes D., Zuman P.: *Trans. Faraday Soc.* **1969**, *65*, 1668.
36. Barnes D., Zuman P.: *Trans. Faraday Soc.* **1969**, *65*, 1681.
37. Ryvolová-Kejharová A., Zuman P.: *J. Electroanal. Chem.* **1969**, *21*, 197.
38. Zuman P., Spritzer L.: *J. Electroanal. Chem.* **1976**, *69*, 433.
39. DeBoer H. S., van Oort W. J., Zuman P.: *Anal. Chim. Acta* **1981**, *130*, 111.
40. Spritzer L., Zuman P.: *J. Electroanal. Chem.* **1981**, *126*, 21.
41. Zuman P.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 254.
42. Zuman P., Barnes D., Ryvolová-Kejharová A.: *Discuss. Faraday Soc.* **1968**, *45*, 20.
43. Zuman P.: *Electroanalysis* **2006**, *18*, 131.
44. Zuman P.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 2548.
45. Zuman P., Barnes D., Ryvolová-Kejharová A.: *Discuss. Faraday Soc.* **1968**, *45*, 202.
46. Zuman P., Horák V.: *Collect. Czech. Chem. Commun.* **1962**, *27*, 187.
47. Zuman P., Turcsanyi B.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 3090.
48. Zuman P., Turscanyi B.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 323.

49. Kakáč B., Mňouček K., Zuman P., Semonský M., Černý A.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 1256.
50. Ryvolová-Kejharová A., Zuman P.: *J. Electroanal. Chem.* **1969**, *21*, 197.
51. Ryvolová-Kejharová A., Zuman P.: *Collect. Czech. Chem. Commun.* **1971**, *36*, 1019.
52. Shibata M., Zuman P.: *J. Electroanal. Chem.* **1997**, *420*, 79.
53. Zuman P., Exner O., Rekker F. R., Nauta W. Th.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 3213.
54. Barnes D., Zuman P.: *Talanta* **1969**, *16*, 975.
55. Barnes D., Uden P. C., Zuman P.: *J. Chem. Soc. B* **1971**, 1114.
56. Barnes D., Zuman P.: *J. Chem. Soc. B* **1971**, 1118.
57. Barnes D., Uden P. C., Zuman P.: *Anal. Lett.* **1970**, *3*, 633.
58. Barnes D., Zuman P.: *J. Electroanal. Chem.* **1973**, *46*, 323.
59. Zuman P.: *J. Electroanal. Chem.* **1977**, *75*, 523.
60. Segretario J., Rusling J. F., Zuman P.: *J. Electroanal. Chem.* **1981**, *117*, 341.
61. Rusling J. F., Segretario J. P., Zuman P.: *J. Electroanal. Chem.* **1983**, *143*, 291.
62. Rusling J. F., Zuman P.: *J. Electroanal. Chem.* **1986**, *213*, 245.
63. Rusling J. F., Zuman P.: *J. Electroanal. Chem.* **1986**, *213*, 255.
64. Rusling J. F., Zuman P.: *J. Electroanal. Chem.* **1986**, *213*, 277.
65. Toure V., Levy M., Zuman P.: *J. Electroanal. Chem.* **1974**, *56*, 295.
66. Fleury M. B., Tohier J., Zuman P.: *J. Electroanal. Chem.* **1983**, *145*, 253.
67. Segretario J. P., Sleszynski N., Zuman P.: *J. Electroanal. Chem.* **1986**, *214*, 259.
68. Segretario J. P., Zuman P.: *J. Electroanal. Chem.* **1986**, *214*, 237.
69. Segretario J. P., Sleszynski N., Partch R. E., Zuman P., Horák V.: *J. Org. Chem.* **1986**, *51*, 5393.
70. Sleszynski N., Zuman P.: *J. Org. Chem.* **1987**, *52*, 2622.
71. Kozlowski J., Zuman P.: *J. Electroanal. Chem.* **1987**, *226*, 69.
72. Kozlowski J., Zuman P. in: *Redox Chemistry and Interfacial Behaviour of Biological Molecules* (G. Dryhurst and I. Niki, Eds), p. 333. Plenum Press, New York 1988.
73. Kozlowski J., Zuman P.: *J. Electroanal. Chem.* **1992**, *343*, 43.
74. Nişli G., Barnes D., Zuman P.: *J. Chem. Soc. B* **1970**, 764.
75. Nişli G., Barnes D., Zuman P.: *J. Chem. Soc. B* **1970**, 771.
76. Nişli G., Barnes D., Zuman P.: *J. Chem. Soc. B* **1970**, 778.
77. Singer S., Zuman P.: *J. Org. Chem.* **1974**, *39*, 836.
78. Hammett L. P.: *Physical Organic Chemistry*, 2nd ed. McGraw–Hill, New York 1970.
79. Zuman P.: *Collect. Czech. Chem. Commun.* **1960**, *25*, 3225.
80. Zuman P.: *Collect. Czech. Chem. Commun.* **1960**, *25*, 3256.
81. Zuman P.: *Ric. Sci.* **1960**, *30*, 229.
82. Kargin J., Manoušek O., Zuman P.: *J. Electroanal. Chem.* **1966**, *12*, 443.
83. Zuman P., Manoušek O., Vig S. K.: *J. Electroanal. Chem.* **1968**, *19*, 147.
84. Zuman P., Bover J., Johnson C. in: *Novel Trends in Electroorganic Synthesis* (S. Torii, Ed.), p. 233. Springer Verlag, Tokyo 1997.
85. Bover W. J., Baymak M. S., Camaione L., Zuman P.: *Electrochem. Commun.* **2003**, *5*, 334.
86. Bover W. J., Johnson D., Baymak M. S., Zuman P.: *Indian J. Chem., Sect. A* **2003**, *42*, 744.
87. Zuman P.: *Chem. Rev.* **2004**, *104*, 3217.
88. Baymak M. S., Vercoe K. L., Zuman P.: *J. Phys. Chem. B* **2005**, *109*, 21928.
89. Salem N., Zuman P.: *Anal. Chem.* **2006**, *78*, 7802.
90. Baymak M. S., Kulla E., Zuman P.: *J. Mol. Liq.* **2007**, *131–132*, 24.

91. Salem N., Andreescu S., Kulla E., Zuman P.: *J. Phys. Chem. A* **2009**, *111*, 4658.
92. Kulla E., Zuman P.: *J. Phys. Chem. A* **2007**, *111*, 12871.
93. Kulla E., Zuman P.: *Org. Biomol. Chem.* **2008**, *6*, 3771.
94. Zuman P.: *Arkivoc, Gen. Pap.* **2002**, ms. 540.
95. Zuman P.: *Chem. Listy* **1951**, *45*, 65.
96. Zuman P.: *Collect. Czech. Chem. Commun.* **1951**, *16*, 510.
97. Zuman P.: *Chem. Listy* **1952**, *46*, 688.
98. Riedl F., Ludvík J., Liška F., Zuman P.: *J. Heterocycl. Chem.* **1996**, *33*, 2063.
99. Ludvík J., Riedl F., Liška F., Zuman P.: *J. Electroanal. Chem.* **1998**, *457*, 177.
100. Zuman P., Bover J., Johnson C. in: *Novel Trends in Electroorganic Synthesis* (S. Torii, Ed.), p. 233. Springer Verlag, Tokyo 1997.
101. Ludvík J., Jirkovský J., Urban J., Zuman P.: *J. Agric. Food Chem.* **1999**, *47*, 3879.
102. Zuman P., Ludvík J.: *Tetrahedron Lett.* **2000**, *41*, 7851.
103. Zuman P., Privman M., Shibata M., Ludvík J.: *Turk. J. Chem.* **2000**, *24*, 311.
104. Ludvík J., Urban J., Jirkovský J., Zuman P.: *Proc. Electrochem. Soc.* **2001**, *2001*, 132.
105. Ludvík J., Zuman P.: *Indian J. Chem., Sect. A* **2003**, *42*, 847.
106. Ludvík J., Riedl F., Urban J., Zuman P.: *Chem. Anal. (Warsaw)* **2004**, *49*, 777.
107. Privman M., Zuman P.: *Heterocycles* **1994**, *37*, 1637.
108. Privman M., Rupp E. B., Zuman P.: *J. Agric. Food Chem.* **1994**, *42*, 2946.
109. Privman M., Zuman P.: *J. Electroanal. Chem.* **1998**, *455*, 235.
110. Smyth W. F., Svehla G., Zuman P.: *Anal. Chim. Acta* **1970**, *51*, 463.
111. Smyth W. F., Svehla G., Zuman P.: *Anal. Chim. Acta* **1970**, *52*, 129.
112. Smyth W. F., Zuman P., Svehla G.: *J. Electroanal. Chem.* **1971**, *30*, 101.
113. Zuman P., Fialek Z.: *J. Org. Chem.* **1991**, *56*, 5486.
114. Zuman P., Shah B.: *Chem. Rev.* **1994**, *94*, 1621.
115. Karakus C., Zuman P.: *J. Electrochem. Soc.* **1995**, *142*, 4018.
116. Zuman P., Fijalek Z.: *J. Electroanal. Chem.* **1990**, *296*, 583.
117. Rupp E., Zhong Q., Zuman P.: *Electroanalysis* **1992**, *4*, 11.
118. Zuman P., Fijalek Z., Dumanović D., Sužnjević D.: *Electroanalysis* **1992**, *4*, 783.
119. Dumanović D., Jovanović J., Sužnjević D., Erceg M., Zuman P.: *Electroanalysis* **1992**, *4*, 795.
120. Rupp E. B., Zuman P., Šestáková J., Horák V.: *J. Agric. Food Chem.* **1992**, *40*, 2016.
121. Dumanović D., Jovanović J., Sužnjević D., Erceg M., Zuman P.: *Electroanalysis* **1992**, *4*, 871.
122. Dumanović D., Jovanović J., Sužnjević D., Erceg M., Zuman P.: *Electroanalysis* **1992**, *4*, 889.
123. Dumanović D., Jovanović J., Marjanović B., Zuman P.: *Electroanalysis* **1993**, *5*, 47.
124. Fijalek Z., Zuman P.: *Electroanalysis* **1993**, *5*, 53.
125. Fijalek Z., Pugia M., Zuman P.: *Electroanalysis* **1993**, *5*, 65.
126. Dumanović D., Kosanović Dj., Zuman P.: *Heterocycles* **1995**, *41*, 1503.
127. Zuman P., Karakus C.: *Denki Kagaku* **1994**, *62*, 1306; *Chem. Abstr.* **1995**, *122*, 186756s.
128. Karakus C., Zuman P.: *J. Electroanal. Chem.* **1995**, *396*, 499.
129. Laviron E., Vallat A., Meunier-Prest R.: *J. Electroanal. Chem.* **1994**, *379*, 427.
130. Manoušek O., Zuman P.: *Chem. Commun.* **1965**, 158.
131. Manoušek O., Zuman P., Exner O.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 3979.
132. Zuman P., Manoušek O.: *Collect. Czech. Chem. Commun.* **1969**, *34*, 1580.
133. Kuder J., Wychick D., Zuman P.: *J. Electroanal. Chem.* **1976**, *71*, 297.

134. Talvik A., Zuman P., Exner O.: *Collect. Czech. Chem. Commun.* **1964**, *29*, 1266.
135. Tang S., Zuman P.: *Collect. Czech. Chem. Commun.* **1963**, *28*, 1524.
136. Zuman P., Chodowski J., Potěšilová H., Šantavý F.: *Nature* **1958**, *182*, 1535.
137. Zuman P., Chodowski J., Šantavý F.: *Collect. Czech. Chem. Commun.* **1961**, *26*, 380.
138. Zuman P.: *Z. Phys. Chem. (Leipzig)* **1958**, Sonderheft, 243.
139. Zuman P.: *Collect. Czech. Chem. Commun.* **1953**, *18*, 36.
140. Zuman P.: *Collect. Czech. Chem. Commun.* **1960**, *25*, 3245.
141. Zuman P.: *Collect. Czech. Chem. Commun.* **1960**, *25*, 3252.
142. Zuman P.: *J. Polarograph. Soc.* **1961**, *7*, 66.
143. Zuman P., Voaden D. J.: *Tetrahedron* **1961**, *16*, 130.25
144. Zuman P.: *Z. Anal. Chem.* **1967**, *224*, 374.
145. Holthuis J. J. M., van Oort W. J., Romkens F. M. G. M., Renema J., Zuman P.: *J. Electroanal. Chem.* **1985**, *184*, 317.
146. Holthuis J. J. M., Vendrig D. E. M. M., van Oort W. J., Zuman P.: *J. Electroanal. Chem.* **1987**, *220*, 101.
147. Zuman P., Holthuis J. J. M.: *Rec. Trav. Chim. Pays-Bas* **1988**, *107*, 403.
148. Brdička R., Zuman P.: *Collect. Czech. Chem. Commun.* **1950**, *15*, 766.
149. Zuman P.: *Collect. Czech. Chem. Commun.* **1951**, *16*, 510.
150. Zuman P., Procházka Z.: *Collect. Czech. Chem. Commun.* **1953**, *18*, 442.
151. Blatná J., Fragner J., Švanda V., Zuman P., Žuffová D.: *Prum. Potravin* **1955**, *4*, 402.
152. Zuman P.: *Collect. Czech. Chem. Commun.* **1954**, *19*, 1140.
153. Bover W. J., Zuman P.: *J. Electrochem. Soc.* **1975**, *122*, 36.
154. Scott W. J., Bover W. J., Bratin K., Zuman P.: *J. Org. Chem.* **1976**, *41*, 1952.
155. Sedon J. H., Zuman P.: *J. Org. Chem.* **1976**, *41*, 1957.
156. Ellaithy M., Veivia D., Zuman P.: *Microchem. J.* **1991**, *43*, 46.
157. van Oort W. J., DeBoer H. S., Zuman P.: *Polarography of Corticosteroids*, p. 541. Elsevier, Amsterdam 1982.
158. Frank A. S., Zuman P.: *Anal. Lett.* **1982**, *15*, 1609.
159. Rusling J. F., Zuman P.: *Heterocycles* **1987**, *26*, 3071.
160. Zuman P.: *Proc. Electrochem. Soc.* **2001**, *2001*, 129.
161. Kapetanović V., Aleksić M., Zuman P.: *J. Electroanal. Chem.* **2001**, *507*, 263.
162. Baymak M. S., Bover W. J., Celik H., Zuman P.: *Electrochim. Acta* **2005**, *50*, 1347.
163. Salem N., Zuman P.: *Anal. Lett.* **2007**, *40*, 2171.
164. Zuman P., Zumanová R., Souček B.: *Collect. Czech. Chem. Commun.* **1953**, *18*, 632.
165. Zuman P., Zumanová R., Souček B.: *Chem. Listy* **1953**, *47*, 140.
166. Zuman P., Fedoroňko M.: *Z. Phys. Chem.* **1958**, *209*, 376.
167. Horn G., Zuman P.: *Collect. Czech. Chem. Commun.* **1960**, *25*, 3401.
168. Fijalek Z., Zuman P.: *Anal. Lett.* **1990**, *23*, 1213.
169. Zuman P., Fijalek Z.: *Anal. Lett.* **1990**, *23*, 1201.
170. Zumanová R., Zuman P.: *Pharmazie* **1954**, *9*, 554.
171. Zuman P., Zumanová R., Teisinger J.: *Collect. Czech. Chem. Commun.* **1955**, *20*, 139.
172. Zuman P., Zumanová R.: *Collect. Czech. Chem. Commun.* **1956**, *21*, 123.
173. Zuman P., Zumanová R.: *Collect. Czech. Chem. Commun.* **1957**, *22*, 929.
174. Zuman P.: *Prace Konf. Polarogr., Warszawa 1956*, p. 339. PWN, Warszawa 1957.
175. Zuman P., Zumanová R.: *Tetrahedron* **1957**, *1*, 28.
176. Koryta J., Zuman P.: *Collect. Czech. Chem. Commun.* **1953**, *18*, 197.
177. Zuman P., Koryta J., Kalvoda R.: *Collect. Czech. Chem. Commun.* **1953**, *18*, 350.

178. Romer M., Donaruma L. G., Zuman P.: *Anal. Chim. Acta* **1977**, *88*, 261.
179. Zuman P.: *Collect. Czech. Chem. Commun.* **1955**, *20*, 649.
180. Zuman P.: *Pharmazie* **1956**, *11*, 449.
181. Smyth W. F., Svehla G., Zuman P.: *Anal. Chim. Acta* **1970**, *51*, 463.
182. Smyth W. F., Svehla G., Zuman P.: *Anal. Chim. Acta* **1970**, *52*, 129.
183. Smyth W. F., Zuman P., Svehla G.: *J. Electroanal. Chem.* **1971**, *30*, 101.
184. Zahradník R., Zuman P.: *Collect. Czech. Chem. Commun.* **1959**, *24*, 1132.
185. Zuman P., Zahradník R.: *Z. Phys. Chem. (Leipzig)* **1957**, *280*, 135.
186. Halls D. J., Townshend A., Zuman P.: *Anal. Chem. Acta* **1958**, *40*, 459.
187. Halls D. J., Townshend A., Zuman P.: *Anal. Chim. Acta* **1968**, *41*, 51.
188. Halls D. J., Townshend A., Zuman P.: *Anal. Chim. Acta* **1968**, *41*, 63.