Translated from *Uspekhi Khimii*, **57**, 228-253 (1988) U.D.C. 541.49;541.128

Metal Complex Catalysis of Electrode Processes

O.N.Efimov and V.V.Strelets

A new field of application of metal complexes for the acceleration of electrode processes is examined. The general principles of the design of metal complex electrocatalytic systems are analysed and the results of studies carried out during the last 10 years on the electrochemical reduction and oxidation of various organic and inorganic substrates are surveyed.
The bibliography includes 177 references.

CONTENTS

I. Introduction 129
II. General principles 129
III. The main electrochemical reactions catalysed by metal complexes 130

I. INTRODUCTION

During the last 30 years, considerable advances have been made in metal complex catalysis (MCC) and have had a strong influence also on other types of catalysis; heterogeneous enzyme catalysis and electrocatalysis. This influence is due to the high theoretical level of understanding of the processes undergone by the substrate in the coordination spheres of metal complexes—in particular, in the case of homogeneous MCC, where it has been possible in many cases to elucidate the sequence of the elementary reactions, to isolate or identify spectroscopically the intermediate compounds, to follow the changes in the oxidation states of the metals during the catalytic process, and to achieve a quantum-chemical description of the character of the bond between the substrate and the metal.[1,2]

Together with the fundamental importance of MCC for the generation of fundamental ideas referring to catalysis as a whole, the practical advantages which it can ensure play a significant role. This applies in the first place to the comparatively mild reaction conditions in solution (low temperature and pressure), low sensitivity to impurities and catalytic poisons, the accessibility of the active centres to the interaction with the substrate, and finally the possibility of controlling the catalytic system by altering the ligand environment of the metal complex and the composition of the medium. In many cases, homogeneous catalysts are superior to heterogeneous catalysts as regards selectivity, being at the same time much more readily available.

The principles of MCC can be readily transferred to the catalysis of electrochemical reactions. In particular, metalloporphyrins have been used successfully to carry out electrocatalytic hydrogen reduction reactions in fuel cells in order to replace or reduce significantly the consumption of expensive metals.[3] However, the application of MCC in electrosynthesis, which has developed most recently, is of greatest interest. One can point out a series of factors which make the combination of MCC with electrochemistry particularly attractive to specialists in both fields. These are in the first place the possibility of replacing at the electrode strong oxidants and reductants, which are frequently expensive and difficult to obtain and furthermore contaminate the reaction mixture by their conversion products. By carrying out a redox reaction at the electrode, it is possible to influence within wide limits its rate by regulating the electrode potential, and to ensure the transfer of any number of electrons without altering the composition of the medium, which is especially important in many-electron reactions. The possibility of lowering the overpotential at the electrode and of increasing the current density by means of MCC are in their turn attractive to electrochemists. Finally, special mention should be made of the fact that MCC can ensure the occurrence of chemical reactions which are altogether impossible in the absence of metal complexes, for example the reduction of nitrogen or carbon monoxide. Furthermore, one should add that the modern methods for the investigation of electrode processes, namely various types of polarography, cyclic voltamperometry, and various pulse methods make it possible to achieve a fairly complete description of the mechanism of the catalysis when combined with electrolysis at a controlled potential and spectroscopic methods.

The statement of the well known electrochemist Baizer[4] that there are unlimited possibilities for an investigator working at the junction of organic chemistry, electrochemistry, and catalysis is fully applicable to metal complex electrocatalysis (MCE). Investigators can use pure methods for the introduction and removal of electrons, procedures for the deposition of potential catalysts on electrode matrices, the advantages of adsorption on electrodes which depends on the electric field, a large set of solvents, and, if necessary, supporting electrolytes which exert a specific influence on the electrode processes and the behaviour of intermediate species in solution.

The trend towards an increase in the number of studies involving the use of metal complexes in electrocatalysis observed in recent years requires systematic treatment of the accumulated data in this essentially new field. It is necessary to understand the methodology of the selection of metal complex electrocatalysts, the general principles of their functioning, and the possibilities and prospects for their use in electrochemical reactions of various substrates. This review is in fact devoted to the consideration of these questions.

II. GENERAL PRINCIPLES

In terms of the mechanism of their action, metal complex catalysts of electrosynthesis can be divided into two main groups. The first includes metal complexes whose coordination spheres remain unchanged throughout the catalytic cycle and electron transfer takes place via an outer sphere mechanism without the formation of an intermediate complex between the substrate (A) and the catalyst (the redox pair P/Q):

$$\begin{gathered} P+e \rightleftharpoons Q, \\ Q+A \rightleftharpoons P+B, \\ B \rightarrow C\ . \end{gathered}$$

It has been suggested that this type of MCE be called redox catalysis.[5] The functions of the redox catalyst (other names: redox transferring agent, mediator) consist in electron transfer from the electrode to the substrate, after which the primary product B of the reduction of the substrate is converted into the final product C already in the course of the chemical reaction. When B is rapidly and irreversibly converted into C, the substrate may be reduced under the conditions of homogeneous electron transfer in the direction opposite to the standard potential drop ($E^0_{P/Q} > E^0_{A/B}$),[6] which greatly extends the scope of redox catalysis. Evidently a gain is achieved using redox catalysts only when they are capable of being rapidly regenerated at the electrode and with high yields at potentials more positive than those of the direct electrochemical reduction of the substrate or less positive than the potentials of its direct electrochemical oxidation, are stable, and can interact rapidly with the substrate. Thus this type of MCE can be usefully employed if, by restorting to homogeneous electron transfer, one increases the rate of the process as a whole by transferring the process to the bulk of the solution and by reducing the overpotential of the electrochemical reaction and also if substrates for which homogeneous redox reactions occur for one reason or another at higher rate than heterogeneous reactions participate in the process.

The second group of catalysts includes metal complexes with the participation of which electron transfer from the electrode to the substrate takes place via an inner sphere mechanism with formation of an intermediate complex between the catalyst and the substrate (PA or QA). The mechanism of the action of these catalyats can be represented in a simplified form by the following schemes:

$$\left.\begin{array}{l}\overrightarrow{P + A \rightleftharpoons PA}\\ PA \xrightarrow{e} PB \rightarrow P + C\end{array}\right|$$

or

$$\left.\begin{array}{l}\overrightarrow{P + e \rightleftharpoons Q}\\ Q + A \rightleftharpoons QA\\ QA \xrightarrow{e} QB \rightarrow P + C\end{array}\right| .$$

Since the reactions of the substrate in the coordination sphere of the metal complex assume the main role in the catalytic cycle, this type of MCE can be usefully defined as coordination electrocatalysis. The electrochemical stage and the chemical reaction of the substrate are coupled with participation of the catalyst–substrate complex and the function of the catalyst consists in the binding and activation of the substrate in the coordination sphere of the metal complex as a result of which the reactivity of the substrate in the electron exchange reaction with the electrode increases. In contrast to redox catalysis, in coordination MCE, P or Q must be coordination-unsaturated or must contain ligands which are kinetically labile in substitution reactions. This is essential for the formation of the intermediate complexes PA and QA.

The choice of a specific metal complex for coordination MCE is appreciably facilitated by the availability of extensive information on the complex formation reactions and activation of substrates which are kinetically inert in redox reactions.[1,2] Having chosen a suitable metal complex which binds the substrate and activates it in its coordination sphere, one can proceed to the solution of practical problems in the coupling of the electrode and chemical reactions. This strategy is evidently idealised but in the subsequent description of this approach it will be illustrated by a number of examples.

In coordination MCE, the metal complex can be immobilised on the electrode surface, for example, by adsorption and special fixing methods,[7] or can be present in the bulk of the solution. The electron exchange between the electrode and the catalyst–substrate complex can then take place either directly or with participation of redox transferring agents. In particular, if the reaction centre in the immobilised coordination catalyst exchanges electrons slowly with the electrode, then the efficiency of this process can be increased by the additional immobilisation on the electrode surface of a redox transferring agent capable of rapid electron exchange both with the electrode and with the reaction centre. As will be shown below, this approach, which has been developed in bioelectrocatalysis for the coupling of enzymes in electrochemical reactions,[8] can be used successfully also in coordination MCE.

In conclusion, we may note that coordination MCE is in fact the only method for the involvement in electrochemical reactions of substrates whose direct oxidation-reduction at the electrode is difficult or does not occur at all. Attention will therefore be concentrated in the present review on precisely this type of MCE.

III. THE MAIN ELECTROCHEMICAL REACTIONS CATALYSED BY METAL COMPLEXES

1. Dehalogenation of Organic Halides

The problem of the dehalogenation of organic halides RX, where R = aryl or alkyl and X = Cl, Br, or I, is of not only theoretical but also of applied importance, because many halides accumulate in the waste from industrial organic synthesis. The direct electrochemical reduction of alkyl and aryl halides is usually carried out at potentials more negative than −1.5 V.†[4] The pattern changes significantly when the complexes of certain transition metals capable of reacting with RX to form more readily reducible compounds are introduced into the electrolyte solution. The reductive dehalogenation of RX can then be performed at considerably more positive potentials, usually at the potentials of the regeneration of the metal complex active in relation to RX. The complexes catalytically active with respect to RX can be arbitrarily divided into three groups: the phosphine, tetra-azamacrocyclic, and polypyridyl complexes. We shall consider each of these groups.

The tetraphosphine complexes of zerovalent nickel $NiPn_4$, electrochemically generated by the two-electron reduction of Ni^{2+} or NiX_2Pn_2 in the presence of an excess of phosphine Pn, catalyse the electrochemical reduction of RX (R = alkyl or benzyl) and ArX (Ar = aryl) with formation of a mixture of the corresponding hydrocarbons (RH or ArH), dimerisation products (R–R or Ar–Ar) and, in the case of alkyl halides, also the alkenes R(−H).[9–11] The reduction takes place at Hg, Pt, Au, or carbon glass cathodes in a diaphragm electrolyser in various solvents [EtOH, tetrahydrofuran (THF), MeCN, etc.]. The ratio of the products depends significantly on the nature of the solvent but not of the electrode. Thus, in the catalytic electrochemical reduction of ArX in an alcoholic medium, the only product is the corresponding ArH, while in THF or in its mixtures with hexamethylphosphoramide (HMP) the product is a mixture of ArH and Ar–Ar, the

† All the potentials are quoted in this review relative to the aqueous saturated calomel electrode.

material yield of biaryl increasing to 70–95% with increase in the HMP content.[9] The electroanalytical study of this reaction permitted the conclusion that the mechanism of the dehalogenation of aryl halides can be represented as schematically as follows:[9]

$$Ni^{2+} \xrightarrow{2e;\ Pn} NiPn_4 \xrightarrow{ArX} ArNiXPn_2 \xrightarrow{2e;\ H^+} Ar^- + NiPn_4,$$
$$Ar^- \xrightarrow{H^+} ArH$$
$$Ar^- + ArNiXPn_2 \rightarrow Ar{-}Ar + X^- + NiPn_4.$$

As a result of the oxidative addition of RX to $NiPn_4$, the intermediate formation of the organonickel σ-derivative $RNiXPn_2$, the stability and further reaction pathways of which depend significantly on the nature of the solvent and the halide, has also been postulated for alkyl halides.[10] Tributyl- and triphenyl-phosphines[9,10] and the diphosphines of the type of bis(diphenylphosphino)ethane (dppe) [12] are used in this reaction.

The study of the mechanism of the electrochemical reduction of 1-iodobutane, 1-iodo-2,2-dimethylpropane, benzyl chloride, and PhBr at an Hg cathode in MeCN in the presence of catalytic amounts of $[Ni(PPh_3)_2(MeCN)_4]^{2+}$ and an excess of PPh_3 led to the conclusion[13] that the active species in relation to RX is also the electrochemically generated $Ni(PPh_3)_4$ and that the subsequent reaction of $RNiX(PPh_3)_2$ (I), formed as a result of oxidative addition, depends on the nature of the organic halide and proceeds in accordance with one of the possible schemes

$$(I) \xrightarrow{e} [RNi(PPh_3)_2X]^- \rightarrow R{-}R + Ni(PPh_3)_4 + X^-,$$
$$(I) \rightarrow Ni(PPh_3)_3X + R^{\cdot} \rightarrow R{-}R + RH + R(-H)$$

via a hydride complex i.e.

$$(I) \rightarrow R(-H) + [Ni(PPh_3)_2(H)X] \rightarrow Ni(PPh_3)_3X + RH + H_2$$

with subsequent electrochemical regeneration of $Ni(PPh_3)_4$. The same complex can promote the electrochemical reduction of allyl halides in MeCN to hexa-1,5-diene with a current yield of 85–95%.[14] The formation of the nickel(I) π-complex $(\pi\text{-}C_3H_5)Ni(PPh_3)Cl$, whose subsequent one-electron reduction is accompanied by the cleavage of the C–Ni bond with regeneration of the catalyst and the formation of the anion X^- and the radical $C_3H_5^{\cdot}$, dimerising with formation of hexadiene, has been proposed as an intermediate in the oxidative addition of the substrate to $Ni(PPh_3)_4$. An important condition for the occurrence of this electrocatalytic reaction is a tenfold excess of PPh_3 relative to Ni^{2+}, which is the initial ion for the preparation of $Ni(PPh_3)_4$.

Together with the diphosphine complexes of nickel, the product of the reversible one-electron reduction $[Rh(dppe)_2]^+$ also exhibits a catalytic activity in the dehalogenation reaction.[15] In the absence of the substrate, the $RH(dppe)_2$ generated electrochemically at the Hg cathode reacts with the solvent [dimethyl sulphoxide (DMSO), MeCN, etc.] to form the hydride $RhH(dppe)_2$, while in the presence of cyclohexyl chloride, a mixture of cyclohexane and cyclohexene is formed. The detection of dicyclohexylmercury as a side product indicates that the reaction proceeds via the intermediate formation of the free cyclohexyl radical.

The phosphine complexes of zerovalent nickel can also be used to carry out more complex reactions with participation of RX. For example, it has been shown[16] that, in *N*-methylpyrrolidinone or a THF–HMP mixture (Au-cathode), the complex $[Ni(Pn_2R'X]^-$, where R′ = ethylene, propene, or styrene and X = Cl, Br, or I, generated by the reduction of Ni^{2+} in the presence of a threefold excess of Pn = PPh_3 and an alkene, reacts with halogenobenzenes to form the corresponding arylalkenes via the mechanism (for example, when R′ = C_2H_4)

$$NiPn_2X_2 + R' \xrightarrow{2e} [NiPn_2R'X]^- \rightleftharpoons \text{«PhNiX»} \xrightarrow{Et_3N} PhCH{=}CH_2 + Ni(0) + Et_3NHX$$

Olefins are arylated as a result of the reversible oxidative addition of PhX with formation of the organonickel complex "PhNiX" of unknown structure, which decomposes irreversibly to form the arylalkene. The process becomes catalytic only in the presence of a base (Et_3N), which apparently promotes the elimination of HX.

Another example of the use of RX for the preparation of more complex products is the electrocatalytic synthesis of arylacetic and arylpropionic acids.[17] These acids are formed as a result of the electrochemical reduction of the corresponding benzyl halides at an Hg cathode in a CO_2-saturated aprotic medium (mixtures of THF with HMP or *N*-methylpyrrolidinone) in the presence of catalytic amounts (10%) of diphosphine complexes of zerovalent nickel or zerovalent palladium. The products are formed via the following proposed mechanism (L = diphosphine):

$$ML_2 \xrightarrow[-L]{RX} RMXL \xrightarrow[-X^-]{2e} RML^- \xrightarrow{CO_2;\ L} RCO_2^- + ML_2$$

The material yield of acids is 20–50% and bibenzyls are formed as side products.

Another group of complexes catalysing the electrochemical reduction of RX consists of square planar nickel(II) and cobalt(II) complexes with tetra-azamacrocycles (L) or Schiff bases. Thus it has been shown[18] that the complexes NiL^{2+} in an aprotic medium [MeCN, dimethylformamide (DMF), DMSO, etc.] undergo reversible one-electron reduction to the stable complexes NiL^+, which undergo an oxidative addition reaction with RX (2-bromo-octane, 2-bromo-2-methylheptane, etc.) to form the organonickel compounds $[RNi(L)Br]^+$ (II), whose subsequent fate depends on the nature of R. For primary RBr, the dehalogenation products RH, R(–H), and R–R are formed as a result of the competing reactions

$$(II) + RBr \rightarrow R{-}R$$

and

$$(II) \xrightarrow{e} R^- \xrightarrow{H^+} RH),$$

while secondary and tertiary RBr are dehalogenated exclusively via the radical mechanism[18]

$$((II) \rightarrow R^{\cdot} \rightarrow RH + R(-H) + R{-}R)$$

The dehalogenation reaction is catalytic and takes place at potentials corresponding to $E^0(NiL^{2+/+})$. It is of interest to note that the introduction of any substituents into L shifts $E^0(NiL^{2+/+})$ to the anodic region, the maximum effect being generated by substituents at the N atoms of the ligand, which makes it possible to lower the RBr reduction potentials down to −1 V.[18] The main products of the dehalogenation of RBr in the presence of nickel(II) complexes of Schiff bases are the corresponding dimers R–R, which shows that the reaction proceeds mainly via a radical mechanism.[19]

The tetra-azamacrocyclic complexes CoL^{2+} [20,21] and the cobalt(II) complexes of Schiff bases[22] exhibit an analogous catalytic activity in the dehalogenation of RX at the potentials of the Co(II/I) redox transition. For example, in the dehalogenation of BuX (X = Cl or Br) in the presence of the electrochemically generated bis(salicylideneiminato)cobalt(I) $[Co(salen)]^-$, the main product is 2-methylpropene. The formation of alkylcobaloxime (sic) [BuCo(salen)] as a side product indicates, according to the authors,[22] the intermediate formation of the butyl radical.

The formation of alkylcobaloximes (sic) [RCo(salen)] in the reaction of $[Co(salen)]^-$ with RX has been used for the electrocatalytic carboxylation of organic halides.[23] Electrolysis of alkyl and benzyl chlorides [R = $PhCH_2$, $Ph(CH_3)CH$, $PhCH{=}CHCH_2$, $CH_3CH{=}CHCH_2$ etc.] at the Hg cathode in the presence of the [Co(salen)] catalyst in a THF–HMP mixture

saturated with CO_2 at atmospheric pressure leads to the formation, after the hydrolysis of the catholyte, of the carboxylic acids RCO_2H in a material yield of 50–97%. In a moist solvent with an H_2O content of $(1–5) \times 10^{-2}$ M, the yield of acids falls somewhat, simultaneously with the appearance in the product of the corresponding RH and R–R. The formation of acids is not observed for aliphatic halides (bromopropane) or bromostyrene, but acids are formed from aryl halides after the replacement of the cobalt complex by $Ni(Ph_3P)_4$. It has been suggested[23] that the formation of acids can be described by the following scheme:

$$[Co\,(salen)] \overset{e}{\rightleftharpoons} [Co\,(salen)]^- \xrightarrow{RX} [RCo\,(salen)] \xrightarrow{2e;\ CO_2} RCO_2^- + [Co\,(salen)]$$

The reaction proceeds either via the intermediate formation of an adduct of CO_2 with alkylcobaloximes or via the attack on CO_2 by the carbonium ion formed on dissociation of [RCo..(salen)]. In the light of these data, it is appropriate to mention a study[24] in which it was shown that the two-electron multistage reduction of alkylcobaloximes [RCo(dmg)Py] (where R = alkyl or benzyl, dmg = dimethyl glyoximate, and Py = pyridine) is accompanied by the formation of a dealkylated cobalt(I) complex whose two-electron reoxidation regenerates the initial alkylcobaloxime in a material yield of 60–95%. In the case of optically active groups R, the oxidation-reduction process involving the initial complex is accompanied by the complete inversion of configuration. A mechanism of the cleavage of the Co–R bond in the reduction of alkylcobaloximes, according to which the axial group R, split off in the form of R$^\cdot$ or R$^-$, remains reversibly bound to cobalt(II) or cobalt (I) complexes as a result of its transfer to the nitrogen atom of the equatorial dmg ligand, has been proposed on the basis of the data obtained. It is quite possible that, in the course of the synthesis of carboxylic acid,[23] the reduction of [RCo(salen)] is also accompanied by the transfer of R to the axial ligand with the simultaneous liberation of a coordination site for a CO_2 molecule. After the coordination and activation of CO_2, the reverse transfer of R takes place, but this time to a CO_2 molecule with formation of a carboxylate ion.

The complexes, which are structural models of vitamin B_{12}, can apparently be used also for involving alkyl halides in other interesting reactions, for example, in reductive cross-coupling. Thus the electrolysis of a mixture of ethyl iodide and acrylonitrile in MeCN at a carbon electrode polymerically modified by the 3,5-diaminobenzoyl derivative of vitamin B_{12} results in the selective formation of valeronitrile.[25] The complex $Ni(teta)^{2+}$ (where teta = hexamethyltetra-azacyclotetradecane) catalyses the electrochemical dehalogenation of RX (for example, 1-bromo-octane) with formation of RH (30%), R–R (45%), and R(–H) (20%).[26,27] After the additional introduction of activated olefins (CH_2 = CHY, where Y = Ar, CN, CO_2Et, etc.) into the catholyte together with RX, the cross-coupling products RCH_2CH_2Y are found to be formed. This reaction is not catalytic, since the complex $[Ni(teta)X_2]^+$ formed is electrochemically inactive.[26]

The third group of compounds catalysing the reductive dehalogenation of RX includes the polypyridyl complexes of Group VIII metals. It has been shown[28,29] that $Co(bipy)_3^{2+}$ (where bipy = 2,2′-bipyridyl) in MeCN catalyses the reductive dimerisation of allyl halides to hexa-1,5-diene. The hexadiene is formed at the redox potentials of $Co(bipy)_3^{2+/+}$, i.e. at potentials more anodic by 1.2 V than the potential of the reduction proper of allyl chloride at a platinum electrode.[29] The oligomers $-[CH_2CH(CH_2Cl)]-_n$ are formed together with the hexadiene. The same reaction can be carried out also in an aqueous medium.[30]

The formation of the hexadiene has likewise been observed in the electrochemical reduction of allyl bromide in MeCN in the presence of $Ni(bipy)_3^{2+}$ and a tenfold excess of the ligand.[31] Alkyl and aryl bromides are dehalogenated with formation of mainly the dimers R–R in DMF in the presence of the $Ni(phen)_3^{2+}$ catalyst (where phen = 1,10-phenanthroline).[32]

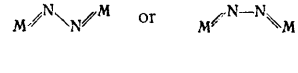
The electrochemical dehalogenation of alkyl and aryl halides can be carried out at a cathode subjected to preliminary modification with the reduction products of the metal complexes. Thus 1-bromo-octane is dehalogenated in DMF in the electrolyser fitted with aluminium electrodes but without a diaphragm, where the cathode is coated by an iron-containing deposit.[33] The dehalogenation of RBr is then achieved at potentials more anodic by 0.9 V than at the aluminium cathode. Under analogous conditions, a cathode coated by the deposit formed in the electrochemical reduction of $Ni(acac)_3$ catalyses the dehalogenation of aryl and benzyl halides.[34]

1,1-Dibromo-2-phenylcyclopropane is dehalogenated with formation of 1-bromo-2-phenylcyclopropane (90%) and phenylallene (10%) in the presence of catalytic amounts of $CrCl_3$. The reduction is carried out at a lead cathode in DMF at the potentials of the $Cr^{3+/2+}$ redox transition, which are more annodic by 2 V than the potentials of the electrochemical reduction proper of the halide.[35] Examples of other reactions involving the electrodehalogenation of organic halides catalysed by metal complexes can be found in Tanaka's review.[36]

2. Reduction of Molecular Nitrogen and Nitric Oxide

The problem of the fixation of nitrogen under mild conditions has attracted the constant attention of investigators during the last 20 years. Although the biological fixation of nitrogen has long been known, the mechanism of this most important reaction remained unknown until recently. The attempts to find simple chemical reactions permitting the reduction of nitrogen to ammonia close to biological conditions have been frequently undertaken, but they encountered difficulties associated with the necessity to rupture the exceptionally strong triple bond in nitrogen (920 kJ mol^{-1}).

Theoretical study has shown[37] that in protic media the most economical pathway (in the sense of energy expenditure) involves the activation of nitrogen in the linear dinuclear complex M...N=N...M, which tends to weaken appreciably the N≡N bond. The best catalytic properties should be manifested by metal ions with the d^3 electronic configuration, for example, Mo^{3+} and V^{2+}. With their participation, the many-electron reduction of nitrogen to N_2H_4 and NH_3 can take place without the intermediate formation of the thermodynamically extremely unfavourable diimide N_2H_2 under conditions with a more uniform distribution of energy among different stages. Such equalisation of the energy relief is achieved by the stabilisation of the intermediates formed in the reduction of nitrogen, as a result of the "conjugation" effect, i.e. the overlap of the *d* orbitals of the metal and the *p* orbitals of nitrogen, for example, in hydrazine derivatives



which have a planar configuration.

The creation of a metal complex electrocatalyst should include the search for a suitable complex M(d^3) capable of activating nitrogen via the coordination mechanism described above and of reacting either directly at the electrode or with participation of a suitable catalytic transferring agent.

The first attempts to set up electrochemical systems for the reduction of nitrogen were based on the use of the nitrogen-fixing hydroxide system $Ti(OH)_3$–Mo(III) in a methanolic alkaline solution. In this system, molybdenum(III) played the role of a catalyst activating nitrogen and titanium(III) played the role of the reductant.[38] The available information about the involvement of a large number of Ti^{3+} ions in electron transfer to the active centre[38] permitted the hope that it would be possible to use Ti^{3+} as the catalytic transferring agent in amalgam or electrochemical reduction. Indeed the introduction of sodium amalgam into the system made it possible to increase appreciably the yields of N_2H_4 and NH_3,[39,40] the formation of nitrogen fixation products being observed already at 20 °C, while in the absence of the amalgam the reaction was carried out at temperatures above 80 °C. The relatively slow reduction of hydrazine in this system and the kinetics of the accumulation of ammonia showed that the fixation products are formed via parallel pathways.[40]

The results obtained in the amalgam reduction of nitrogen made it possible to proceed to direct electrochemical reduction at a mercury cathode in the same system.[41] It was found that the maximum yield of products is attained at a current density of 0.5 mA cm^{-2} or a potential of −1.86 V, i.e. under the conditions for the formation of sodium amalgam on the electrode.[42] At more positive potentials, the rate of reaction decreased exponentially with decrease in the absolute potential, in conformity with the slow discharge theory, while at more cathodic potentials the absorption of charged hydroxide species was hindered. When the mercury cathode was replaced by a rotating amalgamated copper electrode (3000 rev min^{-1}), the electrochemical nitrogen reduction reaction became selective with respect to hydrazine. This was explained[43] by the short contact times between the activated species and the electrode surface as a consequence of which the transfer of six electrons with formation of ammonia became less probable than the four-electron reduction of nitrogen to hydrazine.

The study of the electrochemical behaviour of titanium(III) and titanium(IV) chlorides in methanol made it possible to discover conditions under which the solution remained homogeneous even at a relatively high alkalinity (guanidine buffer, $pK = 13.6$) and titanium(IV) was reduced to titanium(III).[44] The introduction of molybdenum(III) did not affect the homogeneity of the solution. The formation of N_2H_4, catalysed by this system, in electrolysis in a diaphragm electrolyser (a mercury pool at the bottom serving as the cathode at a nitrogen pressure of 30 atm) began at −1.6 V, which corresponded to the half-wave potential for the reduction Ti(IV) + e → Ti(III). The composition of the medium had a significant influence on the rate of reaction.[45,46] The increase in the concentration of alkali as a result of the evolution of hydrogen at the cathode led to a decrease in the rate of formation of N_2H_4, which, however, increased again to the previous value after the introduction of water. It was assumed that the active species in the reduction of nitrogen were heteronuclear titanium(III) and molybdenum(III) complexes; furthermore, the titanium(III) complexes might have played the role of electron transferring agents. The catalytic system containing the components in the proportions Ti/Mo = 3 remained active during electrolysis for more than 14 h.

Similar results were obtained in the amalgam reduction of nitrogen in the titanium(III)–molybdenum(III)–catechol (H_2.Cat) system in an aqueous medium.[47] Catechol forms stable complexes with titanium ions, which remain stable in aqueous media over a wide pH range (from 5 to 13) and which react reversibly at the electrode:

$$Ti(cat)_3^{2-} + e \rightleftharpoons Ti(cat)_3^{3-};\ E^0 = -1.4V.$$

Molybdenum ions also form soluble complexes with catechol, whose composition depends on the pH of the medium and the method of preparation.[48,49] The most active system in the fixation of nitrogen can be obtained by reducing the initial $Ti_2(SO_4)_3$ or Na_2MoO_4 solution with a gradual increase in the alkalinity of the latter from pH 3–4 to pH 7 during electrolysis as a result of the evolution of hydrogen. Under these conditions, the reduction reaction Mo(VI) + e → Mo(V) is accompanied by the dimerisation $2Mo(V) \rightarrow [Mo(V)]_2$ according to polarographic data. The dinuclear dimolybdenum(V) complexes of catechol are reduced irreversibly under the conditions of electrolysis at a controlled potential, forming apparently polynuclear molybdenum(III) complexes. The yield of hydrazine and ammonia in the titanium(III)–molybdenum(III)–catechol system passes through a maximum for the ratio Ti/Mo = 6. In the absence of titanium(III) as well as in all the systems enumerated, molybdenum(III) exhibited a very weak catalytic effect, which made it possible to obtain only traces of hydrazine and ammonia.

The possibility of the electrochemical reduction of nitrogen in aqueous media in the presence of molybdenum complexes was first noted by Zueva et al.[50] However, these data as well as data on the amalgam reduction of nitrogen in methanol solutions, catalysed by molybdenum carbonyl complexes,[51] were poorly reproducible, although the fact itself of the formation of hydrazine was not open to doubt. Reproducible results were achieved using molybdenum(III) complexes as the catalysts, obtained by reducing molybdenum(V) in alkaline methanol solutions in the presence of magnesium ions.[52] The electrochemical[53–55] and kinetic[53,56] study of this system showed that the composition of the species active with respect to nitrogen includes molybdenum(III) and magnesium and that the catalytic complex functions in a state corresponding to its adsorption on the surface, although the catalyst is fairly rapidly deactivated during the reaction. The only nitrogen reduction product was hydrazine.

These results served as a basis in the search for molybdenum(III) complexes capable of being strongly adsorbed on the amalgam surface as a result of the surface activity of the ligand. After numerous surfactants of various nature had been tested, it was possible to observe an appreciable and satisfactorily reproducible increase of the catalytic activity of molybdenum(III) in the presence of dipalmitoylphosphatidylcholine (DPPC).[57] A characteristic feature of the structure of the DPPC molecules, which belong to the class of phospholipids, is a combination of hydrophobic "tails" (palmitic acid residues) with a dipole "head", incorporating the negatively charged phosphate group and the positively charged quaternary ammonium group. Capacitance measurements have shown[58,59] that the DPPC molecules form an adsorption layer on the negatively charged surface of the mercury electrode, being arranged vertically with the "head" towards the surface and the hydrophobic "tails" towards the solution. It has been suggested[56] that the active species is a dinuclear dimolybdenum(III) complex stabilised as a result of interaction with the phosphate (or carbonyl) groups in the adsorbed DPPC. The identical activation energies (~36 kJ mol^{-1}) for the formation of N_2H_4 and NH_3 show that, in the parallel reactions in which these products are formed, there apparently exists a common rate-limiting stage. This stage may be electron transfer from the amalgam to the active complex with formation of a molybdenum derivative of hydrazine (N_2^{4-}). This process is facilitated by the synchronous transfer of protons from the solvent via the hydrophobic layer of DPPC and the formation of the fragment $N_2H_n^{(4-n)-}$. At nitrogen pressures in excess of 50 atm, when the rate of formation of N_2H_4 and NH_3 ceases to depend on pressure, the yield of products calculated relative to the sodium content in the amalgam is approximately 2%.

Further improvement of this catalytic system was achieved by introducing tertiary phosphines, in the presence of which an appreciable catalytic effect was observed already at atmospheric nitrogen pressure.[60] The cocatalytic effect of phosphines was attained only in the presence of a phospholipid; their joint (synergistic) action increased the rate of reaction by a factor of three compared with its rate in the absence of the phospholipid, so that it was virtually identical with the rate of biological fixation of nitrogen (0.1–1 of a N_2 molecule per second per active centre). At a nitrogen pressure of 50 atm, the N_2H_4 concentration reached 2.6×10^{-2} M and the yield relative to the sodium in the amalgam which reacted was 20%.

Recently the fixation of nitrogen in the molybdenum(III)–DPPC–phosphine catalytic system was achieved also under the conditions of electrolysis at a mercury cathode.[61] Although the structure of this multicomponent and most active of all the known nitrogen-fixing systems is still not clear in its details, its investigation by cyclic and a.c. voltamperometry[54,55,62] has to some extent thrown light on the functions of the individual components. Thus it has been suggested that in the adsorption layer there are two types of molybdenum(III) complexes, one of which, containing only molybdenum, binds and activates nitrogen (activator) but exchanges electrons with the electrode only slowly.[62] The second complex—a molybdenum–magnesium complex—does not activate nitrogen but exchanges electrons with the electrode and the activator rapidly and reversibly and thus can function as a redox transferring agent, which is essential for the coupling of the electrochemical and chemical stages of the catalytic process. As a result of the strong adsorption properties of the transferring agent, its concentration on the amalgam surface greatly exceeds the content of the activator. The phospholipid coordinated to the activator increases the degree of adsorption of the layer and approximately equalises the surface concentrations of both components, maintaining them in the proportions optimum for the effective functioning of the catalytic system. The incorporation of the activator in the lipid film specifies a fully defined spatial disposition of the active centre, relative to the electrode on amalgam surface, and, furthermore, it prevents the deactivation of the catalyst during the reaction of the kind observed in the system without a phospholipid.[53] Coordination to phosphines enhances the electron-accepting properties of the transferring agent (and possibly also the activator), which should increase the rate of electron transfer from the amalgam to the substrate. Overall, the creation of a sterically ordered activator–transferring agent–outer electron source (amalgam or electrode) system lowers the energy barrier to electron transfer to the coordinated nitrogen molecule, as a result of which a catalytic effect comparable to the rate of an enzyme process is achieved.

Among other metal complexes catalysing the electrochemical reduction of nitrogen in protic media (water, THF–CH_3OH mixture), mention may be made of the clusters $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$.[63] Electrolysis in the presence of these complexes at $E = -1.7$ V, atmospheric nitrogen pressure, and 20 °C leads to the formation of NH_3 in a current yield of 1.6%.

Mention may also be made of studies on the reduction of N_2 to NH_3 in aqueous hydrochloric acid solutions in the presence of molybdenum complexes and zinc chloride[64] and on the direct reduction of N_2 at an iron cathode in alkaline solutions[65] with a current yield of ammonia not exceeding 1%. The detection of small amounts of ammonia must be checked carefully by carrying out parallel experiments with an inert gas or $^{15}N_2$. Without such a check, there is a possibility of erroneous conclusions about the feasibility of the reduction of nitrogen in particular systems. How likely is the risk of such an error is demonstrated by a study[66] in which it was shown by means of a repeated test in an inert gas atmosphere that the NH_3 detected in the electrochemical and photoelectrochemical reduction of nitrogen at an iron semiconductor (GaP) cathode is formed as a result of the reduction of the admixtures of nitrates and nitrites in the reagents employed. The reduction of nitrogen reported in studies[64,65] where no such check was made is therefore open to doubt.

The main disadvantage of all the electrochemical systems for the reduction of molecular nitrogen known at the present time is the low current yield of ammonia and hydrazine. This is associated with the occurrence of the parallel hydrogen evolution reaction whose rate is significantly higher.

Overall, studies on the electrochemical reduction of nitrogen in protic media are of great theoretical interest and have laid the foundations for future technologies for the synthesis of NH_3 and N_2H_4 under mild conditions. However, it must be recognised that these studied have not so far gone beyond the framework of purely laboratory methods.

Systems incorporating a powerful chemical reductant (organomagnesium, organolithium, and organoaluminium compounds, lithium tetrahydroaluminate, and metallic magnesium) and a transition metal compound capable of forming a complex with molecular nitrogen, which were discovered by Vol'pin and Shur in 1964,[67] served as a basis for the development of a nitrogen reduction process in aprotic media. The final products of the reduction of nitrogen in these systems are compounds of the nitride type, whose hydrolysis can yield ammonia. In the presence of aprotic Lewis acids, the amount of bound nitrogen exceeds by a factor of tens and hundreds the amount of catalyst used.

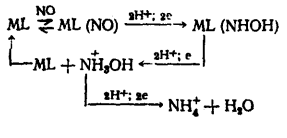
A series of electrocatalytic systems have been proposed,[68] the most effective of which makes it possible to obtain about 3 moles of ammonia per mole of a titanium compound when nitrogen is blown through a cell with an aluminium anode and a nichrome cathode filled with a solution of naphthalene and titanium and aluminium isopropoxides in dimethoxyethane. The reaction mechanism was not investigated, but it has been suggested that naphthalene fulfils the function of a redox transferring agent, aluminium isopropoxide plays the role of the Lewis acid, and the catalyst is the alkoxy-derivative of titanium(II).

A fundamentally new approach to the direct synthesis of organonitrogen compounds, especially aromatic amines,[67] from molecular nitrogen presupposes either the insertion of nitrogen in a metal–aryl bond or direct nucleophilic attack on the nitrogen ligand by a carbanion with subsequent reduction of the ArN=N group coordinated to the metal. Stable diazoalkane, diazenide, and hydrazide derivatives, from which free amines can be isolated by degradative methods, have been obtained by the direct alkylation and acylation of the nitrogen ligand.[69]

The degradative isolation of substituted hydrazines and amines from the hydrazido- and diazenido-complexes of molybdenum and tungsten can be replaced by the electrochemical reduction of these complexes at mercury or platinum cathodes in an aprotic medium using the traces of water in the solvent as the source of protons.[70,71] *N*-Aminopiperidine[70] and 5-amino-4-cyanopyrazole[71] were then obtained in 60–70% yields. Although this approach is very attractive, the problem of creating a continuous catalytic cycle for the synthesis of amines from molecular nitrogen is still far from being solved. The principal difficulties which must be overcome are associated with the appreciable contribution of side reactions and also with the difficulty of regenerating the initial complexes and isolating the target product from the reaction mixture without decomposing the catalytic system.

The interest in the problem of the electrocatalytic reduction of NO is associated with the attempt to utilise under mild conditions the nitrogen oxides contained in the waste gases from many chemical industries. In contrast to the known methods for the heterogeneous reduction of NO with H_2, CO, or NH_3 (see, for example, Seiyama et al.[72]), the electrochemical utilisation of NO does not require high pressures and temperatures. Successful attempts have been made both at the direct electrochemical reduction of NO and at its electrochemical reduction in the presence of metal complexes with formation of N_2O, N_2, NH_2OH, N_2H_4, and NH_3 as the products.[72,73]

In weakly acid aqueous solutions in the presence of transition metal (Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc.) complexes of ethylenediaminetetraacetate (EDTA), the electrochemical reduction of NO at the semiconducting GaAs electrode is accompanied by the selective formation of NH_3 (degree of conversion 22–31%) at room temperature and atmospheric pressure.[74] Similar results have been obtained at a platinum electrode ($E = -1.8$ V) using FeL_3^{2+} complexes (L = phen or bipy) as the catalyst; the degree of conversion of NO into NH_3 is 74–84%.[75] Finally, the selectivity of the conversion of NO into NH_3 at a carbon glass electrode modified with cobaltphthalocyanine reaches 92% (current yield 63%), while at a platinum electrode modified with poly(4-vinylpyridine)iron(II) (a redox catalyst), it does not exceed 2%.[76] This indicates that the reduction of NO proceeds via the coordination, rather than the redox-catalytic, mechanism. Presumably the coordination of NO to the metal is accompanied by a shift of electron density to the NO molecule, which activates it and results in its reduction. The mechanism for the reduction of NO to NH_3 catalysed by a metal complex (ML) can then be represented, for example, in the following manner:[75,77]



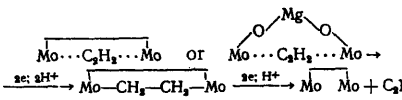
3. Reduction of Compounds with Triple Bonds

The reduction reactions of acetylene, the cyanide ion, nitriles, and isonitriles can be usefully removed to a separate chapter, since they are frequently regarded as model reactions for the reduction of molecular nitrogen, because these substrates are isoelectronic with nitrogen molecule and are in the main electrochemically inactive.

In the series of compounds with multiple bonds whose reduction is catalysed by molybdenum(III) complexes, acetylene is the most convenient substrate for the investigation of the kinetics and mechanism of the electrocatalytic reaction, since the hydrocarbons formed in it can be readily analysed by gas chromatography and the ratio of the products is extremely sensitive to the structure of the catalytically active species. The cysteine complexes of molybdenum(III) catalyse in aqueous solutions (pH 8–10) the electrochemical reduction of acetylene to ethylene and ethane in the proportions $C_2H_4 : C_2H_6 = 0.8$ and in these and other systems, which will be discussed below, ethylene is not reduced and thus ethane is formed from acetylene without the emergence of the ethylene derivative from the coordination sphere of the catalyst.[78,79]

Molybdenum(III) citrate complexes exhibit a similar catalytic activity.[80] It has been suggested[79,80] that a vacancy for the coordination of acetylene (C_2H_2) is liberated as a result of the dissociation of the oxo bridge bonds between the molybdenum(III) ions in the dimeric complex formed on reduction of the initial cysteine or citrate complexes of molybdenum(V). This conclusion agrees well with the fact that the stable complex Na_2MoO_4 (EDTA), in which such dissociation of the bonds after the reduction of molybdenum(VI) to molybdenum(III) does not occur, is catalytically inactive.[79] However, the replacement of the oxo bridges by the more labile sulphide bridges in $Na_2Mo_2O_3S$ (EDTA) or $Na_2Mo_2O_2S_2$ (EDTA) makes the dissociation of the bridge bonds again possible and catalytic activity appears. This entails an increase in selectivity with respect to ethane and the attainable product ratio $C_2H_4 : C_2H_6 = 0.2–0.3$ differs sharply from the ratio characteristic of the cysteine and citrate complexes.

When magnesium ions are introduced into the system containing molybdenum(III) citrate complexes, the current yield of the reaction products becomes quantitative and the selectivity with respect to ethane increases,[80] which suggests that the mutual approach of two molybdenum(III) ions as a result of the appearance of an elongated bridge, made up of a bidentate carboxylate ligand or the magnesium ion, creates a possibility for the linear coordination of C_2H_2 between the molybdenum ions, which is similar to the coordination of nitrogen examined above and favours a more far-reaching reduction of acetylene to ethane via the intermediate dimolybdenum derivative:



In the products of the amalgam reduction of C_2H_2 in the presence of molybdenum(III) and tungsten(III) citrate complexes, appreciable amounts of methane, propane, and propene were detected together with C_2H_4 and C_2H_6.[81,82] The formation of methane (CH_4) indicates an increase in the lifetime of the dimetallic ethane derivative M=CH–CH=M because of the weakening of the proton-donating properties of the medium, as a result of which its further reduction with cleavage of the carbon–carbon bond becomes possible.[81] It has been suggested that this cleavage is accompanied by the formation of carbenoid intermediates of the type $M=CH_2$, whose secondary reactions with C_2H_2 lead to the appearance of propane and propene in the reaction products.[82]

In all the electrocatalytic systems enumerated above, the rate of reaction depended exponentially on the cathode potential and thus the rate-limiting stage is electron transfer from the electroce to the catalytically active species containing a coordinated acetylene molecule. In contrast to this, in the system incorporating the catechol complexes of titanium(III) and molybdenum(III), the rate of reaction no longer depended on the cathode potential and was approximately an order of magnitude higher than in the system without titanium(III).[83] As in the amalgam reduction of nitrogen,[47] it has been suggested that $Ti(cat)_3^{3-}$ functions as the catalyst transferring electrons from the electrode to the catalytically active species in the bulk of the solution.

The iron-molybdenum cofactor isolated from nitrogenase has been used[84] as the catalyst for the electrochemical reduction of C_2H_2. The main product of electrolysis at a mercury cathode in the borate buffer (pH 9.6) at $E = -1.8$ V was C_2H_4 with a current yield of 2%. Nitrogenase also catalysed this reaction but only in the presence of adenosinetriphosphate and methylviologen as the catalytic transferring agent, since the direct electron transfer from the electrode to the active centre of the enzyme was prevented by its protein environment.

The stoichiometric reaction involving the reduction of C_2H_2 to C_2H_4 by a synthetic analogue of ferredoxin containing a cluster with the cubane structure, i.e.

$$2\,[Fe_4S_4(SR)_4]^{3-} + C_2H_2 + 2H^+ \rightarrow 2\,[Fe_4S_4(SR)_4]^{2-} + C_2H_4\ ,$$

where R = Ph or p-MeC_6H_4,[85] has been used to set up an electrocatalytic cycle in which the reduced form of the cluster was constantly regenerated at a mercury cathode:[86]

$$2\,[Fe_4S_4(SR)_4]^{2-} \overset{2e^-}{\rightleftharpoons} 2\,[Fe_4S_4(SR)_4]^{3-} \xrightarrow{C_2H_2;\ 2H^+} 2\,[Fe_4S_4(SR)_4]^{2-} + C_2H_4\ .$$

The conclusions concerning the role of iron sulphide and iron molybdenum sulphide clusters in the electrocatalytic reactions must be treated with caution, since the dissociation or decomposition of the cluster into low-molecular-weight fragments is possible in their reduction. In particular, in methanolic solutions of $FeCl_2$ (or $FeCl_3$) and Li_2S, sodium amalgam reduces C_2H_2 to C_2H_4 and C_2H_6 with an activity close to that of the cluster $[Fe_4S_4(SBu)_4]^{2-}$, which decomposes under the conditions of amalgam reduction.[87]

The modification of the surface of the electrode prepared from polymeric sulphur nitride $(SN)_x$ by molybdenum ions (possibly via their binding to the surface sulphur atoms) made it possible to obtain an electrode on which acetylene was selectively reduced to ethylene with a quantitative current yield and which exhibited an activity exceeding that of nitrogenase.[88]

Electrocatalytic systems based on molybdenum complexes have also been used to reduce other substrates with triple bonds. Thus, in the presence of molybdenum(III) citrate complexes at a mercury cathode at a potential of −1.8 V, the cyanide ion is reduced to NH_3 and CH_4; furthermore, C_2 and C_3 hydrocarbons are produced in smaller amounts.[89] In the reduction of CH_3CN in the same system, propane and propene were found together with the main products C_2H_6 and NH_3, which indicates the dissociation of the C–C bond in the activated CH_3CN molecule with the intermediate formation of, apparently, the carbenoid fragment $Mo{=}CH_2$ and the growth of the carbon chain in its interaction with the next CH_3CN molecules.[90] The formation of amines in these systems was not observed.

The iron sulphide and iron molybdenum sulphide clusters already mentioned catalyse the reduction, in a protic medium, of methyl isonitrile to CH_4, C_2H_4, and C_2H_6 and of acetonitrile to C_2H_6 and NH_3.[91] Under the same conditions, the azide ion is reduced to N_2H_4, NH_3, and N_2,[92] while N_2H_4, NH_3, and RNH_2 are formed from RN_3 (R = CH_3 or HOC_2H_4).[93] The reduction can be carried out, in particular, in an aqueous borate buffer solution (pH 10) at a chemically modified electrode prepared by depositing the $(Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$ cluster from solution in acetonitrile onto the surface of an electrically conducting support. However, the activity of this electrode decreases with time as a consequence of the deposition of the cluster from the electrode surface.[93]

4. Reduction of Carbon Oxides

The creation of catalysts for the low-temperature reduction of carbon monoxide and dioxide is of potentially very great importance, since, as the coal, petroleum, and natural gas resources are exhausted, carbon monoxide may becomes a source of raw material for the synthesis of various organic compounds.

A review has been devoted[94] to questions of the coordination chemistry of CO_2 and its biological, chemical, photochemical, and electrochemical activation. The amalgam or electrochemical reduction of CO_2 in the absence of metal complexes can lead to various products of the type of formate,[95] oxalate,[95,96] and many other organic compounds (tartrate, glycolate, etc.),[94] depending on the conditions (the material of the electrode, solvent, etc.).

The purely electrochemical reduction of CO_2 is an energy consuming process, since the formation of the radical-anion $CO_2^{\cdot-}$, which is the primary product of the conversion of CO_2, takes place at potentials of approximately −2 V.[94] The situation may change significantly when metal complex catalysts are used. The possibility of involving CO_2 in the electrolytic carboxylation of organic halides was already mentioned previously.[17] Another reaction catalysed by metal complexes is the reduction of CO_2 to CO. The tetra-azamacrocyclic complexes of cobalt[97] and nickel,[98] $Re(bipy)(CO)_3Cl$,[99] $[Ru(bipy)_2.(CO)_2]^{2+}$,[100] RhL_2Cl (where L = diphosphines),[101] etc. serve as catalysts. The reaction is carried out in aqueous organic or aqueous media at atmospheric or elevated CO_2 pressures at different electrodes (mercury, carbon glass, platinum, etc.). The reduction prduct is the CO + H_2 mixture and under optimum conditions the current yield of CO reached 90–100%. In an alkaline medium, formate is formed together with CO.[100]

The electrolysis is carried out at the electrochemical reduction potentials of the metal complexes. In all cases, these potentials are more cathodic than the thermodynamic potentials of the reduction of CO_2 to CO.[94] The metal complexes retain their catalytic activity for a long time.[98–101] It has been suggested[99] that they play the role of redox catalysts in this reaction. However, it may be thought that, since this reaction is in fact the reverse of the metal complex-catalysed conversion reaction of water gas (CO + H_2O),[102] the function of the catalyst consists not only in electron transfer from the electrode to the CO_2 molecule but also in preliminary coordination and activation of the latter. The absence of formate from the products indicates, according to the authors,[99] that hydride derivatives capable of reducing CO_2 to formate are not formed in the reduction of the metal complexes.

The complex $Rh(bipy)_2^+$, electrogenerated from $[Rh(bipy)_2.(CF_3SO_3)]^{2+}$ in acetonitrile at the potentials of the $Rh(bipy)_2^{0/-}$ redox transition (E^0 = −1.55 V), reduces CO_2 catalytically at atmospheric pressure to formate with a current yield of 64%.[103] The formation of the product is described by a stoichiometric scheme with participation of the cations of the supporting electrolyte Bu_4N^+:

$$Bu_4N^+ + CO_2 \overset{2e^-}{\rightarrow} HCO_2^- + Bu_3N + CH_2{=}CHEt\ .$$

It was shown in the same study that the complex Ru(trpy).(dppe) [where trpy = 2,6-di(2-pyridyl)pyridine], electrogenerated by the irreversible two-electron reduction of $Ru(trpy)(dppe)Cl^+$, catalyses, under analogous conditions at E = −1.4 V, the reduction of CO_2 in accordance with the stoichiometric scheme

$$Bu_4N^+ + 2CO_2 \overset{2e^-}{\rightarrow} Bu_3N + CH_2{=}CHEt + CO + HCO_3^-\ .$$

It is suggested that the catalytic activity of metal polypyridyl complexes is due to the possibility of their electrochemical reduction accompanied by the ejection of the $CF_3SO_3^-$ or Cl^- anions and the appearance in the coordination sphere of a free site for the binding of CO_2. The subsequent reduction of CO_2 in the coordination sphere leads to products whose nature depends significantly on the basicity of the intermediates in the reduction of CO_2. The polypyridyl ligands, which play the role of a kind of "electron reservoir", apparently have an important function in the catalytic activity of these complexes.[103]

The cluster $[Fe_4S_4(SR)_4]^{2-}$ (where R = Ph or $PhCH_2$), which has the cubane structure and is a model of ferredoxin, catalyses in DMF at $E = -1.7$–2.0 V the electrochemical reduction of CO_2 on mercury with formation of formate, oxalate, and carbon monoxide as the products.[104] The same products are formed also in the non-catalytic electrochemical reduction of CO_2 but at much more cathodic potentials (−2.4 V). Furthermore, whereas the non-catalytic reduction of CO_2 leads mainly to the oxalate, the principal product in the catalytic process is formate (selectivity up to 93%). By varying the composition of the electrolyte, it is possible to drive the process towards the required product.

Thus the use of transition metal compounds capable of forming complexes with CO_2 can ensure the operation of a particular catalytic reduction mechanism. The reduction of CO_2 to formaldehyde, methanol, and hydrocarbons is more promising. For a number of reasons, it is desirable to carry out the reaction in protic media. Only the first steps have been taken along these lines. Thus it has been shown[105] that reduction of CO_2 with zinc amalgam catalysed by VO^{2+} ions in acid aqueous solutions (pH 2.5) leads to the formation of formaldehyde, methanol, and methane together with formic acid. In the presence of titanium ions, aluminium amalgam reduces CO_2 selectively to CH_2O alone under the usual conditions.[106] The reaction proceeds within a narrow pH range in the vicinity of 3.5, which enabled the authors[106] to put forward the hypothesis that the catalytically active species is formed by the association of two titanium ions.

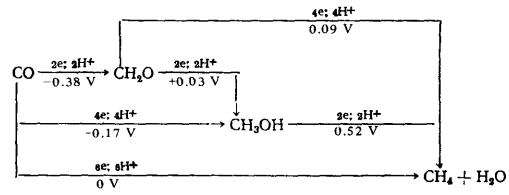
The molybdenum(III) complex of catechol catalyses the electrochemical reduction of CO_2 at a mercury cathode to C_1–C_3 hydrocarbons.[107] The reduction was carried out in an aqueous buffer solution (pH 7) under the conditions of galvanostatic electrolysis (i = 7 mA cm^{-2}). The reaction is accompanied by the vigorous evolution of hydrogen and the overall yield of hydrocarbons does not exceed 0.2%. It is of interest that the formation of oxygen-containing products of the reduction of carbon dioxide (CO, CH_2O, HCO_2H, and CH_3OH) was not observed and the rate of reaction increased by a factor of 5 after the introduction into the system of $Ti(cat)_3^{3-}$, which is itself inactive in relation to CO_2. It has been suggested that CO_2 is reduced in the coordination sphere of Mo(III) via a mechanism involving inner sphere catalysis without the emergence of intermediates into the bulk of the system. This system is of interest also because outer sphere redox catalysis takes place in it together with the inner-sphere catalysis, since $Ti(cat)_3^{3-}$ fulfils the function of an agent transferring electrons from the cathode,[47,83] The formation of C_1–C_3 hydrocarbons was observed also in the reduction of CO_2 catalysed by $[Fe_4S_4(SR)_4]^{2-}$.[104]

Other classes of transition metal complexes catalysing the electrochemical reduction of CO_2 are metallophthalocyanines and metalloporphyrins. This question has been considered in greatest detail by Tarasevich and Radyushkina.[3] The main reduction products are oxalic and gluconic acids. One may also mention a study[108] in which it was shown that $VO(acac)_2$ in acetonitrile catalyses the electrochemical reduction of CO_2 at the potentials at which the corresponding vanadium(II) complex is generated, but the reduction products were not identified.

Thus the possibility of the formation of complexes of CO_2 with transition metal compounds and the possibility of the inner sphere electron transfer to the coordinated CO_2 molecule at much more anodic potentials than in the purely electrochemical reduction demonstrate that MCE is promising in various carbon dioxide conversion reactions.

The involvement of carbon monoxide in catalytic reactions leading to the synthesis of organic compounds has long formed an industrial application. It is sufficient to point out the processes involving the formation of synthol via the Fischer–Tropsch reaction, the carbonylation of methanol with formation of acetic acid, the conversion of water gas, etc.[2] On the other hand, the reactions involving the electrochemical conversion of CO began to be investigated comparatively recently. This is because the electrochemical reduction of carbon monoxide takes place at extremely negative potentials, since the thermodynamics of this process are apparently determined primarily by the potential corresponding to the reduction of CO to the radical-anion $CO^{\cdot-}$. Thus CO can be reduced chemically only with the Na–K alloy in THF.[109] After the hydrolysis of the reaction mixture, the glycolate and oxalate anions as well as $C_3O_3^{2-}$ are then formed as the final products. The electrochemical reduction of CO at pressures of several hundreds of atmospheres at a steel cathode under the conditions of galvanostatic electrolysis leads to the formation of squaric acid $C_4O_4H_2$.[110] Apparently, in liquid ammonia (−50 °C), in the presence of 0.1 M KI, carbon monoxide is reduced at various cathodes at potentials close to the potentials at which the solvated electron (e_S^-) is generated.[111] However, the attempt at a preparative electrochemical reduction of CO under these conditions failed. Only the reduction of CO by electrogenerated e_S^- leads to the formation of the dimeric anions $C_2O_2^{2-}$, which are precipitated as a deposit of the salt $K_2C_2O_2$.

The use of many-electron reactions should significantly improve the energetics of the reduction of carbon monoxide. The thermodynamics of the reduction of CO to the simplest organic compounds confirms this.

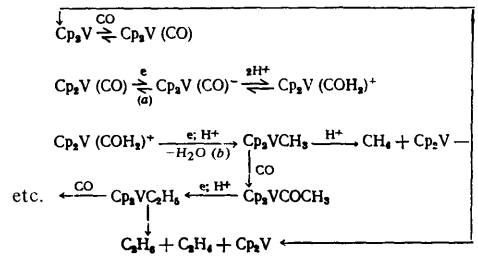


Despite the favourable thermodynamics, the direct amalgam or electrochemical reduction of CO at a mercury cathode is impossible, apparently because of kinetic limitations. The picture changes significantly when CO is coordinated to transition metal complexes, i.e. under the conditions of coordination electrocatalysis, where the catalyst–substrate complex with an activated CO molecule is reduced.

The fruitfulness of this approach was first demonstrated in relation to the vanadocene-catalysed amalgam reduction of CO with formation of C_1–C_4 hydrocarbons.[112–116] It was shown[112,113] that Cp_2V effectively catalyses the reduction of CO with sodium amalgam even at room temperature and atmospheric CO pressure in aprotic solvents (DMF, THF, etc.) containing diethylbarbituric acid or a phenol as the proton donor. The main product is methane (85–95%) and the remainder consists mainly of saturated C_2–C_4 hydrocarbons. Under optimum conditions, more than 100 molecules of hydrocarbons are formed per catalyst molecule and the periodic introduction of consumable reagents into the system (amalgam, CO, and a proton donor) makes it possible to achieve a continuous process.[112] This reaction is a kind of electrochemical analogue of the Fischer–Tropsch synthesis, proceeding with participation of the adsorbed catalyst and being characterised by the transfer of the first electron to the coordinated substrate molecule in the direction opposite to that of the standard potential drop, since $E^0[Cp_2V(CO)^{0/-}] = 2.3$ V and the amalgam potential is approximately −2.1 V.[114] We may note that this is the first case of endoergic electron transfer[6]

in MCE, known to us, which has been demonstrated experimentally. Vanadocene also catalyses the evolution of oxygen, as a result of which the current yield of hydrocarbons does not exceed 10%.[114]

Both reactions (the reduction of CO and the evolution of H_2) take place in the adsorption layer without the emergence of the intermediate reduction products into the bulk of the solution and their kinetics is described taking into account the surface and not the bulk-phase concentration of the catalyst. Carbon monoxide is reduced at potentials which are insufficient for the intermediate formation of the hydride Cp_2VH^-, which makes it possible to rule out the hydride mechanism of the reduction of CO and explains the absence of CH_2O and CH_3OH from the reaction products.[113,114] Finally, the formation of C_2–C_4 hydrocarbons and also the growth of the hydrocarbon chain in the Fischer–Tropsch synthesis take place as a result of the insertion of CO in the metal–alkyl bond in the intermediate alkyl complexes Cp_2V–Alk,[115] which yet again indicates the retention of the general characteristics of MCC in electrocatalysis. The catalytic cycle of the vanadocene-catalysed electrochemical reduction of CO can be represented schematically as follows:[115,116]



Stage (*a*) is endoergic and occurs because of the presence in the cycle of the rapid and irreversible stage (*b*) in which the C–O bond is ruptured.

The efficiency of metal complex electrocatalytic systems depends significantly on the stability of the catalyst. Thus, together with vanadocene, other electrochemically generated metallocenes of Group VB and VIB metals likewise catalyse the electrochemical reduction of CO in aprotic solvents containing proton donors, but the catalytic activity of systems based on them decreases to zero fairly rapidly.[117] This is due to the metastability of the complexes Cp_2M (M = Nb, Mo, or W) responsible for the coordination of CO.

The advantage of electrocatalytic reactions in theoretical research consists in the possibility of using electrochemical methods for their investigation. For the electrochemical reduction of CO catalysed by metallocene dichlorides, it has been possible not only to identify by electrochemical methods the primary products of the interaction of the catalyst with CO and to reach a conclusion about the nature of the catalytic activity of the species, but also to elucidate the cause of the differences between the catalytic activities of the complexes Cp_2MCl (M = Ti, V, Nb, Mo, or W), which consists in the different stabilities of the metallocenes or their cations responsible for the coordination of CO, and also to characterise the kinetic thermodynamic regions where these are stable.[117,118] The thermodynamics of the region corresponding to the stability of catalysts is an important factor which must be taken into account in the development of metal complex electrochemical systems. Without taking it into account, one can over-reduce or, conversely, oxidise the catalyst, which would alter the electronic configuration of its constituent metal, making it unfavourable for the coordination of the substrate, so that the catalyst loses its activity. The studies where the possibility of predicting the thermodynamic stability of neutral and ionic metal complexes on the basis of tabulated ionisation potentials of the corresponding metals has been demonstrated in relation to sandwich and wedge-sandwich metal complexes, catalytically active in numerous reactions,[67,122] merit attention in this connection.[119–121]

The electrochemical reduction of CO to C_1–C_3 hydrocarbons can be achieved also in aqueous solution ($6 < pH < 13$) using the catechol complex of molybdenum(III) adsorbed on the mercury cathode as the catalyst.[123] As in non-aqueous media, the main product is methane (80–90%) and the overall current yield of hydrocarbons is a fraction per cent, since the main bulk of the electricity is consumed in the parallel H_2 evolution reaction catalysed by the same molybdenum(III) complexes. The efficiency of this system increases appreciably after the introduction of $Ti(cat)_3^{3-}$, which is manifested by an increase in the rate of reaction and in the current yield of the hydrocarbons to 15%.[124] The kinetic and electrochemical studies of this system have led to the conclusion that the catalytic species in relation to CO is a carbonyl complex of molybdenum(III) and the reversible $Ti(cat)_3^{2-/3-}$ pair functions as a redox catalyst. Thus, when a redox catalyst is introduced into the system, electron transfer also to molybdenum(III) complexes, activating the CO molecule but having no direct contact with the electrode, becomes possible as a result of which the overall rate of reaction increases. This is an excellent example of the combination of coordination catalysis [activation and inner-sphere reduction of CO in the presence of the molybdenum(III) complex] and redox catalysis [electron transfer by the $Ti(cat)_3^{3-}$ complex to the molybdenum(III) carbonyl complex] which leads to an increase in the catalytic efficiency of the system.

The electrocatalytic reduction of CO by metal complexes can yield not only hydrocarbons but also oxygen-containing products. At room temperature and atmospheric pressure, CO is reduced selectively in aqueous solutions (pH 3.5) to methanol at a platinum electrode modified by the complex $[Fe^{II}(CN)_6]Fe^{II}K_2$ (A) at $E = -0.9$ V.[125–127] Methanol is also formed at a non-polarised cathode, the process being accompanied by the oxidation of the complex (A) to $Fe^{II}(CN)_6 . Fe^{III}K$ (B). It has been suggested that the CO molecule is activated as a result of its incorporation into the coordination sphere of the anion $[Fe(CN)_6^{4-}]$ with displacement of CN^- and the formation of $[Fe(CN)_5(CO)]^{3-}$ and the subsequent reduction of CO in MeOH via a redox catalytic mechanism [the catalyst is the (A)/(B) redox pair].[125,126]

There are relatively few data on the electrochemical oxidation of CO catalysed by metal complexes. One can only mention a study[128] where it was shown that in aqueous solutions of HX (X = Cl, Br, or I) the complex $[Rh(CO)_2X_2]^-$ catalyses the oxidation of CO to CO_2 on carbon glass at potentials of approximately 0.4 V. This reaction is thought to be promising for use in fuel cells.

5. Oxidation of Water and Organic Compounds

The oxidation of water to oxygen is a complex many-electron process, which gives rise to certain requirements to be met by the metal complex catalyst of this reaction, which are extremely similar to the requirements imposed on the catalysts of the reduction of nitrogen: it is necessary that the metal complex should be able to "switch over" the reaction from the thermodynamically unfavourable one-electron mechanism to the more favourable many-electron mechanism.[129–131] Only then do the thermodynamics of the overall oxygen formation reaction become sufficiently favourable. By analogy with natural photosynthesis, it has been suggested[129]

that the metal complex should consist of a dinuclear or tetranuclear cluster, each atom of which is capable of accepting respectively two electrons or one electron, such acceptance being reversible since only then is it possible to achieve an efficient operation of the catalyst. Polynuclear complexes can also be used, but in this case the oxidation of water would proceed via the intermediate formation of a peroxy-derivative. However, this would happen only if the metal atom in the complex is capable of changing its valence by two units.

The use of such approaches[132,133] showed that simple hydroxo-complexes of iron(II) and cobalt(II) are effective catalysts of the electrochemical oxidation of water. This is due to the ability of these metals to change their valence by two units with formation of highly reactive M(IV) complexes, oxidising water to the peroxide, which is rapidly oxidised further under these conditions or decomposes catalytically at the electrode, affording oxygen. The mechanism of the electrocatalytic oxidation of water with participation of hydroxo-complexes of iron and cobalt (MOH^+) can be represented by the scheme[132,133]

$$M^{II}OH^+ \xrightleftharpoons{2OH^-} M^{II}(OH)_3^- \xrightarrow{-2e} M^{IV}(OH)_3^- \rightarrow M^{II}OH^+ + H_2O_2 \quad . \qquad (1)$$

The catalytic process is apparently of a mixed bulk-phase–surface character although the appearance of a catalytic oxidation wave on the voltage–current plots even at Fe^{2+} and Co^{2+} concentration in the range 10^{-8}–10^{-6} M indicates a significant contribution of the bulk-phase process.[132]

The development of catalysts for the oxidation of water is important also from the standpoint of the solution of the problem of its photocatalytic oxidation. In particular, using iron and cobalt hydroxo-complexes, some of the first catalytic systems for the oxidation of water with high quantum yields under the influence of visible light have been developed.[134,135] Detailed kinetic study led to the conclusion[136–139] that the mechanism of the catalytic action of the hydroxo-complexes in the reactions involving the oxidation of water by one-electron oxidants is more complex than the one represented by the overall Eqn.(1).

In subsequent studies, whose authors attempted to use the complexes of the same transition metals but with other ligands are homogeneous catalysts of the electrochemical and chemical oxidation of water, the high activity of even traces of the hydroxo-complexes led, in our view, to an erroneous interpretation of the data obtained. Thus it has been concluded[140] that the hypothetical complex $[Fe(bipy)_2(bipyH)(OH)]^+$ is a catalyst of the electrochemical oxidation of water. However, here no account was taken of the fact that in alkaline media the initial complex $Fe(bipy)_3^{2+}$ hydrolyses with formation of amounts of $FeOH^+$ which are quite sufficient for the appearance of a catalytic effect.[132] An analogous error was most probably made also by Zamaraev and Parmon[141] and Nord et al.[142] in studies of the chemical oxidation of water by one-electron oxidants. The solutions of iron and cobalt complexes with various ligands which they used as "catalysts" almost always contain traces of the corresponding hydroxo-complexes or hydrolyse with their formation. It has been shown[143,144] that such trace amounts are entirely sufficient for the observed catalytic effect.[141,142]

It has been reported[145,146] that the dinuclear complex $[(bipy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bipy)_2]^{4+}$ (C) oxidises water to oxygen during its electrochemical four-electron oxidation to $[(bipy)_2(O)Ru^{V}ORu^{V}(O)(bipy)_2]^{4+}$ in an acid medium. However, the authors note that the initial complex is destroyed during the catalytic reaction. It is entirely possible that the complex $RuO_2.xH_2O$, which is known to catalyse effectively the chemical and electrochemical oxidation of water to oxygen in an acid medium,[147] is formed in the course of the degradation. Furthermore, the complex (C) catalyses the chemical or electrochemical reactions in which Cl^- is oxidised to Cl_2.[148,149] In particular, this has been the cause of the erroneous conclusion[145] that the dimer (C) is catalytically active in the electrochemical oxidation of water, since traces of Cl^- ions were present in the electrolyte solution.

Thus, despite certain advances associated with the detection of the catalytic activity of the hydroxo-complexes or iron(II) and cobalt(II),[132,133] the problem of the development of metal complex catalysts for the electrochemical oxidation of water is still far from being solved.

Organic compounds can be oxidised with participation of a number of transition metal ions in the highest oxidation states (Co^{3+}, Ce^{4+}, MnO_4^-, Mn^{3+}, $Cr_2O_7^{2-}$, Tl^{3+}). Some of these reactions can be used to set up an electrocatalytic cycle in which the transition metal ion is regenerated in the initial state by oxidation at the anode. It is by no means always convenient to regenerate the oxidant in the presence of the substrate and this operation is frequently performed in a separate electrolyser and the substrate is then oxidised in another reactor. Analysis of the reactions using electrochemically generated oxidants is outside the framework of the present review. The necessary information about this question can be secured from a monograph[150] and another review.[151] We shall deal only with two examples of the use of metal complexes in oxidation reactions. One of them refers to the application of polypyridyl complexes of ruthenium(IV) as the catalytic transferring agents in the oxidation of organic compounds (S) [152] in accordance with the mechanism

$$[(trpy)(bipy)RuO]^{2+} + S + H_2O \rightarrow [(trpy)(bipy)RuOH_2]^{2+} + S{=}O$$
$$\uparrow \quad -2e;\ -(E = 0.6\text{–}0.8\ V) \quad \downarrow$$

The oxidation is carried out in a diaphragm electrolyser at a carbon glass anode in phosphate (pH 7) or borate (pH 9) buffer solutions at a metal complex concentration of about 10^{-3} M. Under these conditions, it is possible to oxidise 2-propanol to acetone, toluene to benzoic acid, *p*-xylene to terephthalic acid, and cyclohexene to *p*-benzoquinone via the intermediate formation of 2-cyclohexanone. The oxidation can be carried out using not only a dissolved metal complex but also one which was immobilised beforehand on the anode surface.[153]

The second example refers to the cathodic reactions in which oxygen is activated with participation of metal complexes or transition metal ions. Such activation can be achieved by reducing oxygen to hydrogen peroxide and regenerating from the latter the $OH^{\cdot}$ radical via the reaction of H_2O_2 with Fe^{2+} ions (Fenton's reagent). Electrocatalytic systems for the oxidation of polymethylbenzenes to the corresponding aldehydes[154] and also of aliphatic C_5–C_{30} hydrocarbons and 3-methylpentane to ketones[155] have been constructed in accordance with this principle. The electrolysis is carried out in hydrochloric acid solutions at a mercury cathode, the solution being saturated with oxygen. The following mechanism of the catalytic cycle has been proposed:[154]

$$Fe^{3+} \xrightarrow{e} Fe^{2+} \rightarrow Fe^{3+} + OH^{\cdot} \xrightarrow[-H_2O]{PhCH_3} PhCH_2^{\cdot} \xrightarrow{O_2}$$
$$O_2 \xrightarrow{2e;\ 2H^+} H_2O_2 \rightarrow$$
$$\rightarrow PhCH_2OO^{\cdot} \rightarrow PhCHOOH \xrightarrow[-Fe^{3+};\ -OH^{\cdot}]{Fe^{2+}} PhCHO \quad .$$

The electrochemical activation of oxygen in hydrocarbon oxidation reactions has been achieved also via electron transfer to an iron–porphyrin complex deposited on the surface of a graphite electrode.[156] The electrode was impregnated with a benzene solution of iron-tetraphenylporphyrin chloride and

dried *in vacuo*. Hexane and 1,2-dimethylcyclohexane were oxidised to the corresponding hexanols under the conditions of potentiostatic electrolysis at $E = -1.5$ V in acetonitrile containing 10% of the hydrocarbon and 5×10^{-2} M acetic anhydride. The current yield of the alcohol was 7%. During the electrolysis, the system lost its activity and after 2 h the reaction ceased completely because the iron-porphyrin was completely washed off the cathode. It has been suggested that the oxidation of hydrocarbons (RH) at this electrode is described by the following consecutive reaction scheme (Pr = porphyrin):

$$\begin{array}{c} \mathrm{PrFe^{III} \xrightarrow{e} PrFe^{II} \xrightarrow{e} PrFe^{I}} \\ \downarrow O_2 \qquad \downarrow O_2 \\ \mathrm{PrFe^{III}O_2^- \xrightarrow{e} PrFe^{III}O_2^{2-} \xrightarrow[-AcO^-]{Ac_2O} PrFe^{III}OOAc \xrightarrow{-AcO^-}} \\ \rightarrow [\mathrm{PrFe^{IV}=O}]^+ \xrightarrow{KH} \mathrm{PrFe^{III}} + \mathrm{ROH}. \end{array}$$

The oxo-complex $[PrFe^{IV}=O]^+$ serves as the hydrocarbon oxidising agent. Overall, the catalytic cycle can be regarded as an electrochemical model of cytochrome P-450.

---o0o---

Thus the use of metal complexes in the catalysis of electrode processes make it possible to reduce the energy consumption and to ensure the occurrence of electrochemical reactions of substrates which are electrochemically inactive or are discharged at electrodes with a high overpotential. The metal complex-catalysed reductive dehalogenation reactions are promising for practical applications, in particular, for the decontamination of waste water containing toxic organic halides and for the solution of certain problems in fine organic synthesis, including the synthesis of carboxylic acids from alkyl and aryl halides and carbon dioxide. The successful development of catalysts for the electrochemical oxidation of nitrogen and carbon monoxide, which make it possible to reduce these substrates at low cathodic potentials and to increase thereby the current yield of the products, enables us to count on fundamentally new possibilities in the electrosynthesis of hydrazine from N_2 and of organic compounds from CO (i.e. a raw material which is non-traditional for electrochemistry) at low pressures and temperatures. The use of metal complexes for the catalysis of electroprocesses in photoelectrochemical solar energy converters (catalysts of the oxidation of water) and current sources (catalysts of the reduction of CO and CO_2 and also of the oxidation of alkanes and CO) is also promising, although one must admit that the development of catalysts for these processes has not as yet gone beyond the framework of laboratory research.

The results presented in this review demonstrate only a small fraction of the possibilities which have arisen in metal complex electrocatalysis with a skilful combination of the principles of electrochemistry and homogeneous and heterogeneous catalysis with ideas derived from modern inorganic and organometallic chemistry. One may hope that the development of this undoubtedly promising field will lead to the discovery of many fundamentally new catalytic reactions and may possibly serve for the creation of new industrial processes.

During the preparation of the present review, there has been a sharp growth of the number of studies on the electrocatalytic reduction of CO_2 to CO. The complexes $\{Pd[PhP.(CH_2CH_2PPh_2)_2]R_3P\}^{2+}$ (where R = MeO, Et, Ph, or CH_2OH),[157] $Ni(bipy)_3^{2+}$, $Ni(dppe)_3^{2+}$,[158] $Re(CO)_3LCl$ (where L = bipy and its substituted derivatives),[159–162] Ni(teta)$^+$, and Co(salen)[163] have been used as catalysts in acetonitrile in the presence of various proton donors. Significantly more attention has been devoted in these studies to the electroanalytical investigation of the mechanism of the catalytic action of the metal complexes. In particular, it has been shown[157] that the key stage in the electrocatalytic cycle is the insertion of CO_2 in the Pd–H bond of the hydride complex formed as an intermediate in the electrochemical reduction. It has been noted[159,161,162] that the efficiency of the catalytic action and the stability of the complexes fixed on electrode-supports by electropolymerisation methods, by incorporation in a polymer matrix, etc. is significantly enhanced. The electrodes modified with an insoluble $K_2Fe[Fe(CN)_6]$ film catalyse the reduction of CO_2 and CO to methanol in an aqueous medium in the presence of water-soluble iron, nickel, cobalt, and chromium complexes.[164,165] The complex $Ru(bipy)_2.(CO)_2^{2+}$ catalyses the selective reduction of CO_2 to $HCOO^-$ in acetonitrile in the presence of $Me_2H_2N^+$ or PhOH as proton donors.[166] Individual examples of the catalysis of CO_2 reduction reactions and also of the dehalogenation of RX by phosphine, polypyridyl, and macrocyclic nickel complexes may be found in Troupel's paper.[167]

The possibility, in principle, of reducing nitrogen by protonating the complex $[W(N_2)_2(dppe)_2]$ with toluene-*p*-sulphonic acid in THF with subsequent electrochemical reduction of the resulting hydrazido-cation $[W(NNH_2)(p\text{-}MeC_6H_4SO_3).(dppe)]^+$ in an atmosphere of N_2 with formation of NH_3 and the regeneration of the initial dinitrogen complex has been demonstrated.[168,169] The products of the reduction of Cp_2TiCl_2 in THF and methanol catalyse the electrochemical reduction of N_2 to NH_3.[170] The current yield of ammonia does not exceed 1.5% and the results have not been confirmed by blank experiments (in an argon atmosphere) in experiments using $^{15}N_2$.

In an aqueous medium, macrocyclic cobalt and nickel complexes catalyse the electrochemical reduction of NO_3^- to hydroxylamine,[171] while water-soluble iron porphyrinates catalyse the reduction of NO_2^- to N_2O, NH_3, and NH_2OH;[172,173] the nitrosyl complex [Fe(NO)Pr] has been proposed to an intermediate in the last reaction.[173] A review[174] has been devoted to the consideration of the electrochemical oxidation reactions of organic compounds, H_2O, Cl^- and the reduction of NO_2^- catalysed by polypyridyl complexes of ruthenium and osmium. Other reviews[175–177] deal with studies in which metal complexes are used as redox transferring agents.

REFERENCES

1. C.Masters, "Homogeneous Transition-metal Catalysis: A Gentle Art" (Translated into Russian), Izd.Mir, Moscow, 1983.
2. H.Henrici-Olivé and S.Olivé, "Coordination and Catalysis" (Translated into Russian), Izd.Mir, Moscow, 1980.
3. M.R.Tarasevich and K.A.Radyushkina, "Kataliz i Elektrokataliz Metalloporfirinami" (Catalysis and Electrocatalysis by Metalloporphyrins), Izd.Nauka, Moscow, 1982.
4. M.M.Baizer (Editor), "Organic Electrochemistry" (Translated into Russian), Izd.Mir, Moscow, 1976.
5. C.P.Andrieux, J.-M.Dumas-Bouchiat, and J.M.Saveant, J.Electroanal.Chem., 1978, **87**, 39.
6. V.G.Mairanovskii, "Elektrosintez Monomerov" (Electrosynthesis of Monomers), Izd.Nauka, Moscow, 1980, p.244.
7. R.W.Murray, Acc.Chem.Res., 1980, **13**, 135.
8. A.I.Yaropolov and I.V.Berezin, Uspekhi Khim., 1985, **54**, 1448 [Russ.Chem.Rev., 1985(9)].

9. M.Troupel, J.Robin, S.Sibille, et al., J.Chem.Res. Synop., 1980, 26.
10. S.Sibille, J.C.Folest, J.Coulombeix, et al., J.Chem. Res.Synop., 1980, 268.
11. M.Troupel, J.Robin, S.Sibille, et al., J.Chem.Res. Synop., 1980, 24.
12. O.Sock, M.Troupel, J.Perichon, et al., J.Electroanal. Chem., 1985, **183**, 237.
13. G.Schiavon, G.Bontempelli, and B.Corain, J.Chem. Soc., Dalton Trans., 1981, 1074.
14. G.Bontempelli, S.Daniele, and M.Fiorani, J.Electroanal, Chem.Interfacial Electrochem., 1984, **160**, 249.
15. J.A.Sofranko, R.Eisenberg, and J.A.Kampmeier, J.Amer.Chem.Soc., 1979, **101**, 1042.
16. M.Troupel, J.Robin, G.Meyer, and J.Perichon, Nouv. J.Chim., 1985, **9**, 487.
17. J.F.Fauvarque, A.Juttand, C.Chevrot, et al., French Appl.2 530 266; Ref.Zhur.Khim., 1985, 1L329.
18. J.Y.Becker, J.B.Kerr, D.Pletcher, and R.Rosas, J.Electroanal.Chem., 1981, **117**, 97.
19. C.Gosden, J.B.Kerr, D.Pletcher, and R.Rosas, J.Electroanal.Chem., 1981, **117**, 101.
20. C.Gosden, J.B.Kerr, D.Pletcher, and R.Rosas, J.Electroanal.Chem., 1981, **117**, 135.
21. D.C.Olson and J.Vasilevskis, Inorg.Chem., 1969, **8**, 1611.
22. A.Puzeddu, G.Costa, and N.Marsich, J.Chem.Soc., Dalton Trans., 1980, 1489.
23. J.C.Folest, J.M.Duprilot, J.Perichon, et al., Tetrahedron Lett., 1985, **26**, 2633.
24. M.D.Le Hoang, Y.Robin, J.Devynck, et al., J.Organomet.Chem., 1981, **222**, 311.
25. A.Ruhe, L.Walder, and R.Scheffold, Helv.chim.acta, 1985, **68**, 1301.
26. K.P.Healy and D.Pletcher, J.Organomet.Chem., 1978, **161**, 109.
27. K.P.Healy and D.Pletcher, J.Organomet.Chem., 1980, **186**, 401.
28. S.Margel and F.S.Anson, J.Electrochem.Soc., 1978, **125**, 241.
29. S.Margel and F.S.Anson, J.Electrochem.Soc., 1978, **125**, 1232.
30. J.F.Rusling and G.N.Kaman, J.Electroanal.Chem., 1985, **187**, 355.
31. H.Bontempelli, S.Daniele, and M.Fiorani, Ann.chim. (Ital.), 1985, **75**, 19.
32. W.H.Smith and Y.-M.Huo, J.Electroanal.Chem., 1985, **188**, 189.
33. J.L.Hall, R.D.Geer, and P.W.Jennings, J.Org.Chem., 1976, **41**, 719.
34. J.L.Hall, R.D.Geer, and P.W.Jennings, J.Org.Chem., 1978, **43**, 4364.
35. R.Wolf and E.Steekhan, J.Electroanal.Chem., 1981, **130**, 367.
36. H.Tanaka, Yuki Gosei Kataku Kyokaishi (J.Synth. Org.Chem.Japan), 1985, **43**, 511.
37. A.E.Shilov, "Novoe v Khimicheskoi Fiksatsii Azota" (Advances in the Chemical Fixation of Nitrogen), Izd.Mir, Moscow, 1983, p.132.
38. N.T.Denisov, A.E.Shilov, N.I.Shuvalova, and T.P.Panova, React.Kinet.Catal.Lett., 1975, **2**, 237.
39. O.N.Efimov, A.A.Brikenshtein, A.E.Shilov, and V.P.Sinel'nikova, USSR P.535 210; Byul.Izobret., 1976(42), 44.
40. G.V.Nikolaeva, O.N.Efimov, A.A.Brikenshtein, and N.T.Denisov, Zhur.Fiz.Khim., 1976, **50**, 3030 [Russ. J.Phys.Chem., 1976(12)].
41. O.N.Efimov, V.N.Tsarev, and A.A.Brikenshtein, Zhur.Fiz.Khim., 1977, **51**, 1200.
42. A.V.Gorodyskii, V.V.Danilin, O.N.Efimov, et al., React.Kinet.Catal.Lett., 1979, **11**, 337.
43. A.V.Gorodyskii, V.V.Danilin, N.E.Nechaeva, and O.N.Efimov, React.Kinet.Catal.Lett., 1980, **15**, 373.
44. S.I.Kulakovskaya and O.N.Efimov, Zhur.Fiz.Khim., 1979, **53**, 1057 [Russ.J.Phys.Chem., 1979(4)].
45. S.I.Kulakovskaya, L.P.Vasilieva, and O.N.Efimov, React.Kinet.Catal.Lett., 1980, **14**, 181.
46. G.V.Nikolaeva, S.I.Kulakovskaya, O.N.Efimov, and A.E.Shilov, Kinetika i Kataliz, 1985, **26**, 473.
47. G.N.Petrova, O.N.Efimov, and N.T.Denisov, Izv. Akad.Nauk SSSR, Ser.Khim., 1985, 1683.
48. L.M.Charney and F.A.Schultz, Inorg.Chem., 1980, **19**, 1527.
49. L.M.Charney, H.O.Finklea, and F.A.Schultz, Inorg. Chem., 1982, **21**, 549.
50. A.F.Zueva, O.N.Efimov, A.D.Styrkas, and A.E.Shilov, Zhur.Fiz.Khim., 1972, **46**, 760 [Russ.J. Phys.Chem., 1972(3)].
51. A.E.Shilov, A.K.Shilova, and T.A.Vorontsova, React. Kinet.Catal.Lett., 1975, **3**, 143.
52. L.P.Didenko, A.G.Ovcharenko, A.E.Shilov, and A.K.Shilova, Kinetika i Kataliz, 1977, **18**, 1078.
53. L.P.Didenko, A.E.Shilov, and A.K.Shilova, Kinetika i Kataliz, 1979, **20**, 1488.
54. L.Pospisil and L.P.Didenko, J.Electroanal.Chem., 1985, **184**, 209.
55. L.Pispisil, L.P.Didenko, and A.E.Shilov, J.Electroanal.Chem., 1986, **197**, 305.
56. L.P.Didenko, O.K.Gavrilina, E.E.Yablonskaya, et al., Nouv.J.Chem., 1983, **7**, 605.
57. L.P.Didenko, A.K.Shilova, and A.E.Shilov, Dokl. Akad.Nauk SSSR, 1980, **254**, 643.
58. L.Pospisil, J.Kuta, E.Müller, and H.Dörfler, J.Electroanal.Chem., 1980, **106**, 359.
59. S.I.Kulakovskaya, O.N.Efimov, and L.P.Didenko, Bioelectrochem.Bioenerg., 1984, **13**, 7.
60. A.K.Shilova, V.D.Makhaev, and A.E.Shilov, Dokl. Akad.Nauk SSSR, 1984, **277**, 1414.
61. V.V.Strelets, A.B.Gavrilov, V.N.Tsarev et al., Kinetika i Kataliz, 1986, **27**, 332.
62. V.V.Strelets, A.B.Gavilov, and L.Pospisil, J.Electroanal.Chem., 1986, **210**, 173.
63. K.Tanaka, T.Takanak, and Y.Hozumi, Chem.Lett., 1982, 1203.
64. B.V.Rao, K.R.Upadrashta, A.Baradarajan, and M.Satyanarayana, Indian Chem.Eng., 1984, **26**, 21.
65. A.Schlafani, V.Augugliaro, and M.Schiavello, J.Electrochem.Soc., 1983, **130**, 734.
66. M.Hallman, J.Electroanal.Chem., 1984, **181**, 307.
67. M.E.Vol'pin and V.B.Shur, "Novoe v Khimicheskoi Fiksatsii Azota" (Advances in the Chemical Fixation of Nitrogen), Izd.Mir, Moscow, 1982, p.77.
68. E.E.Van Tamelen, Acc.Chem.Res., 1970, **3**, 361.
69. J.J.Lee, "Novoe v Khimicheskoi Fiksatsii Azota" (Advances in the Chemical Fixation of Nitrogen), Izd.Mir, Moscow, 1982, p.231.
70. C.J.Pickett and G.J.Leigh, J.Chem.Soc., Chem.Comm., 1981, 1033.
71. H.M.Colquhoun, A.E.Crease, and S.A.Taylor, J.Chem. Soc., Chem.Comm., 1983, 1158.
72. T.Seiyama, M.Mizumoto, T.Ishihara, and N.Yamazoe, Ind.Eng.Chem.Process Des.Dev., 1979, **18**, 279.
73. S.H.Langer and K.T.Rate, Ind.Eng.Chem.Process. Des.Dev., 1983, **22**, 264.
74. K.Ogura and M.Takagi, J.Electroanal.Chem., 1985, **183**, 277.
75. K.Ogura and H.Ishikawa, J.Chem.Soc., Faraday Trans.I, 1984, **80**, 2243.

76. K.Ogura and S.Yamasaki, J.Appl.Electrochem., 1985, **15**, 279.
77. S.Uchiyama and G.Muto, J.Appl.Electrochem., 1981, **11**, 275.
78. M.Ichikawa and S.Mesitsuka, J.Amer.Chem.Soc., 1973, **95**, 3411.
79. F.A.Schultz, D.A.Ledwith, and L.O.Leazenbee, "Electrochemical Studies of Biological Systems", ACS Ser.No.38, New York, 1977, p.78.
80. G.N.Petrova, A.F.Zueva, O.N.Efimov, and V.V.Strelets, Zhur.Fiz.Khim., 1978, **52**, 3155 [Russ.J.Phys. Chem., 1978(12)].
81. V.V.Strelets, V.M.Rudakov, and O.N.Efimov, J.Electroanal.Chem., 1979, **95**, 103.
82. V.V.Strelets, V.N.Tsarev, and O.N.Efimov, Kinetika i Kataliz, 1981, **22**, 359.
83. G.N.Petrova, O.N.Efimov, and O.A.Tutochkina, Izv. Akad.Nauk SSSR, Ser.Khim., 1988, 36.
84. G.N.Petrova, L.N.Uzenskaya, L.A.Syrtsova, and O.N.Efimov, Elektrokhimiya, 1980, **16**, 1079.
85. R.S.McMillan, J.Renaud, J.G.Reinolds, and R.H.Holm, J.Inorg.Biochem., 1979, **11**, 213.
86. K.Tanaka, M.Tanaka, and T.Tanaka, Chem.Lett., 1981, 895.
87. A.I.Yarkevich, L.A.Nikonova, and A.E.Shilov, Izv. Akad.Nauk SSSR, Ser.Khim., 1982, 2394.
88. J.F.Robinson, T.D.Behymer, and H.B.Mark, J.Amer. Chem.Soc., 1982, **104**, 1224.
89. G.N.Petrova and O.N.Efimov, Elektrokhimiya, 1980, **16**, 1078.
90. G.N.Petrova, A.F.Zueva, and O.N.Efimov, Elektrokhimiya, 1981, **17**, 888.
91. K.Tanaka, Y.Imasaka, M.Tanaka, et al., J.Amer. Chem.Soc., 1982, **104**, 4258.
92. Y.Imasaka, K.Tanaka, and T.Tanaka, Chem.Lett., 1983, 1477.
93. S.Kuwabata, Y.Hozumi, K.Tanaka, and T.Tanaka, Chem.Lett., 1985, 401.
94. R.Ziessel, Nouv.J.Chim., 1983, **7**, 613.
95. B.R.Egging and J.McNeill, J.Electroanal.Chem., 1983, **148**, 17.
96. Yu.B.Vasiliev, V.S.Bagotskii, N.V.Osetrova, et al., 1985, **189**, 271.
97. B.Fisher and R.Eisenberg, J.Amer.Chem.Soc., 1980, **102**, 7361.
98. M.Beley, J.-P.Collin, R.Ruppert, and J.-P.Sauvage, J.Chem.Soc., Chem.Comm., 1984, 1315.
99. J.Hawecher, J.-M.Lehn, and R.Ziessel, J.Chem.Soc., Chem.Comm., 1984, 328.
100. H.Ishida, K.Tanaka, and T.Tanaka, Chem.Lett., 1985, 405.
101. S.Slater and J.H.Wagenknecht, J.Amer.Chem.Soc., 1984, **106**, 5367.
102. E.G.Chepaikin and M.L.Khidekel', "Koordinatsionnaya Khimiya" (Coordination Chemistry), 1982, Vol.8, p.1011.
103. C.M.Bolinger, B.P.Sullivan, D.Conrad, et al., J.Chem. Soc., Chem.Comm., 1985, 796.
104. M.Tezuka, T.Yajima, A.Tsuchiya, et al., J.Amer. Chem.Soc., 1982, **104**, 6834.
105. R.G.Sadkova, E.N.Sal'nikova, and A.P.Khrushch, Kinetika i Kataliz, 1976, **17**, 1613.
106. E.N.Sal'nikova, A.P.Khrushch, M.L.Khidekel', and A.E.Shilov, Kinetika i Kataliz, 1980, **21**, 278.
107. G.N.Petrova and O.N.Efimov, Elektrokhimiya, 1983, **19**, 948.
108. M.Kitamura, A.Kitani, and K.Sasaki, Denki Kagaku, 1978, **46**, 603.
109. P.W.Lendor and P.C.Versloot, J.Chem.Soc., Chem. Comm., 1983, 284.
110. G.Silvestri, S.Gambino, G.Filardo, et al., Electrochim. Acta, 1978, **23**, 413.
111. F.A.Uribe, P.R.Sharp, and A.J.Bard, J.Electroanal. Chem., 1983, **152**, 173.
112. V.V.Strelets, V.N.Tsarev, and O.N.Efimov, Dokl. Akad.Nauk SSSR, 1981, **259**, 646.
113. V.V.Strelets and V.N.Tsarev, Kinetika i Kataliz, 1983, **24**, 73.
114. V.V.Strelets and V.N.Tsarev, Kinetika i Kataliz, 1984, **25**, 821.
115. V.V.Strelets and V.N.Tsarev, Kinetika i Kataliz, 1985, **26**, 1344.
116. V.V.Strelets and V.N.Tsarev, "Tezisy Dokladov IV Mezhdunarodnogo Simpoziuma po Gomogennomu Katalizu" (Abstracts of Reports at the IVth International Symposium on Homogeneous Catalysis), Leningrad, 1984, Vol.4, p.204.
117. V.V.Strelets, S.V.Kukharenko, and V.N.Tsarev, Kinetika i Kataliz, 1987, 258.
118. V.V.Strelets, S.V.Kukharenko, G.L.Soloveichik, et al., Kinetika i Kataliz, 1985, 1484.
119. V.V.Strelets and S.V.Kukharenko, Dokl.Akad.Nauk SSSR, 1984, **275**, 894.
120. V.V.Strelets and S.V.Kukharenko, Nouv.J.Chim., 1984, **8**, 785.
121. S.V.Kukharenko, G.L.Soloveichik, and V.V.Strelets, Izv.Akad.Nauk SSSR, Ser.Khim., 1986, 1020.
122. G.L.Soloveichik and B.M.Bulychev, Uspekhi Khim., 1983, **52**, 72 [Russ.Chem.Rev., 1983(1)].
123. G.N.Petrova, O.N.Efimov, and V.V.Strelets, Izv. Akad.Nauk SSSR, Ser.Khim., 1982, 2608.
124. G.N.Petrova, O.N.Efimov, and V.V.Strelets, Izv. Akad.Nauk SSSR, Ser.Khim., 1983, 2042.
125. K.Ogura and S.Yamasaki, J.Chem.Soc., Faraday Trans.I, 1985, **81**, 267.
126. K.Ogura and H.Watanabu, J.Chem.Soc., Faraday Trans.I, 1985, **81**, 1569.
127. K.Ogura and M.Kaneko, J.Molec.Catal., 1985, **31**, 49.
128. J.Wu and C.P.Kubiak, J.Amer.Chem.Soc., 1985, **105**, 7456.
129. N.N.Semenov, G.I.Likhtenshtein, and A.E.Shilov, Dokl.Akad.Nauk SSSR, 1975, **221**, 1374.
130. A.E.Shilov, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1977, **22**, 521.
131. V.Ya.Shafirovich and A.E.Shilov, Kinetika i Kataliz, 1982, **23**, 1311.
132. V.V.Strelets, O.N.Efimov, and V.Ya.Shafirovich, Kinetika i Kataliz, 1977, **18**, 646.
133. V.Ya.Shafirovich and V.V.Strelets, Nouv.J.Chim., 1978, **2**, 199.
134. V.Ya.Shafirovich, N.K.Khannanov, and V.V.Strelets, Nouv.J.Chim., 1980, **4**, 81.
135. N.K.Khannanov and V.Ya.Shafirovich, Dokl.Akad. Nauk SSSR, 1981, **260**, 1418.
136. N.K.Khannanov, A.V.Khramov, A.P.Moravskii, and V.Ya.Shafirovich, Kinetika i Kataliz, 1983, **24**, 858.
137. A.P.Moravskii, N.K.Khannanov, A.V.Khramov, et al., Khim.Fiz., 1984, **3**, 1584.
138. A.Harriman, G.Porter, and P.Walters, J.Chem.Soc., Faraday Trans.II, 1981, **77**, 2373.
139. P.K.Ghosh, B.S.Brunschwig, M.Chou, et al., J.Amer. Chem.Soc., 1984, **106**, 4772.
140. A.T.Fal'kengof, V.A.Bogdanovskaya, M.R.Tarasevich, et al., Dokl.Akad.Nauk SSSR, 1984, **275**, 388.
141. K.I.Zamaraev and V.N.Parmon, Uspekhi Khim., 1983, **52**, 1433 [Russ.Chem.Rev., 1983(9)].

142. G.Nord, B.Pedersen, and E.Bjergbakke, J.Amer. Chem.Soc., 1983, **105**, 1913.
143. N.K.Khannanov and V.Ya.Shafirovich, Kinetika i Kataliz, 1981, **22**, 248.
144. N.Sutin and C.Creutz, Pure Appl.Chem., 1980, **52**, 2717.
145. S.W.Gertsen, G.J.Samuels, and T.J.Meyer, J.Amer. Chem.Soc., 1982, **104**, 4029.
146. J.A.Gilbert, D.S.Eggleston, W.R.Murphy, et al., 1985, **107**, 3855.
147. M.Grätzel, Acc.Chem.Res., 1981, **14**, 376.
148. C.D.Ellis, J.A.Gilbert, W.R.Murphy, and T.J.Meyer, J.Amer.Chem.Soc., 1983, **105**, 4842.
149. W.T.Vining and T.J.Meyer, J.Electroanal.Chem., 1985, **195**, 183.
150. M.Ya.Fioshin and M.G.Smirnova, "Elektrokhimicheskie Sistemy v Sinteze Khimicheskikh Produktov" (Electrochemical Systems in the Synthesis of Chemical Products), Izd.Khimiya, Moscow, 1985.
151. I.A.Avrutskaya and G.A.Kokarev, "Elektrosintez i Bioelektrokhimiya" (Electrosynthesis and Bioelectrochemistry), Izd.Nauka, Moscow, 1975, p.34.
152. M.S.Thompson, W.F.De Giovani, B.A.Moyer, and T.J.Meyer, J.Org.Chem., 1984, **49**, 4972.
153. W.Kutner, T.J.Meyer, and R.W.Murray, J.Electroanal. Chem., 1985, **195**, 375.
154. R.Tomat and A.Rigo, J.Appl.Electrochem., 1979, **9**, 301.
155. R.Tomat and A.Rigo, J.Appl.Electrochem., 1985, **15**, 167.
156. A.B.Sorokin, A.M.Khenkin, and A.A.Shteinman, "Fundamental Research in Homogeneous Catalysis" (Edited by A.E.Shilov), Gordon and Breach Sci. Publ., New York, 1986, Vol.2, p.745.
157. D.L.DuBois and A.Miedaner, J.Amer.Chem.Soc., 1987, **109**, 113.
158. S.Daniele, P.Ugo, G.Bontempelli, and M.Fiorani, J.Electroanal.Chem., 1987, **219**, 259.
159. A.I.Breikss and H.D.Abruna, J.Electroanal.Chem., 1986, **201**, 347.
160. C.R.Cabrera and H.D.Abruna, J.Electroanal.Chem., 1986, **209**, 101.
161. S.Cosnier, A.Deronzier, and J.-C.Moutet, J.Electroanal.Chem., 1986, **207**, 315.
162. T.R.O'Tolle, L.D.Margerum, and T.D.Westmoreland, J.Chem.Soc., Chem.Comm., 1985, 1416.
163. D.J.Pearce and D.Pletcher, J.Electroanal.Chem., 1986, **197**, 317.
164. K.Ogura and M.Takagi, J.Electroanal.Chem., 1986, **206**, 209.
165. K.Ogura, J.Appl.Electrochem., 1986, **16**, 732.
166. H.Ishida, H.Tanaka, K.Tanaka, and T.Tanaka, J.Chem.Soc., Chem.Comm., 1987, 131.
167. M.Troupel, Ann.Chim.(Ital.), 1986, **76**, 151.
168. C.J.Pickett and J.Talarmin, Nature, 1986, 652.
169. C.J.Pickett, K.S.Ryder, and J.Talarmin, J.Chem.Soc., Dalton Trans., 1986, 1453.
170. J.Y.Becker, S.Avraham, and B.Posin, J.Electroanal. Chem., 1987, **230**, 143.
171. I.Taniguchi, N.Nakashima, and K.Yasukouchi, J.Chem. Soc., Chem.Comm., 1986, 1814.
172. M.H.Barley, M.R.Rhodes, and T.J.Meyer, Inorg. Chem., 1987, **26**, 1746.
173. M.H.Barley, K.J.Takauchi, and T.J.Meyer, J.Amer. Chem.Soc., 1986, **108**, 5876.
174. T.J.Meyer, J.Electrochem.Soc., 1984, **131**, 221C.
175. H.Lund, J.Molec.Catal., 1986, **38**, 203.
176. E.Steckham, Angew.Chem., 1986, **25**, 683.
177. S.Torii, Synthesis, 1986, 873.

Division of the Institute
of Chemical Physics,
USSR Academy of
Sciences, Chernogolovka