Coordination Chemistry Reviews, 99 (1990) 15–53
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

METAL COMPLEX CATALYSIS OF ELECTROCHEMICAL REACTIONS

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(Received 13 September 1988)

CONTENTS

A. INTRODUCTION

In the past 30 years, significant progress has been made in the field of metal complex catalysis (MCC), which has had a strong influence on heterogeneous and enzyme catalysis and on electrocatalysis. This influence is the result of a good theoretical understanding of the processes taking place with the substrate in the coordination sphere of metal complexes, especially for homogeneous catalysis, where it proved possible in a number of cases to ascertain the sequence of elementary reactions, to discern or identify spectrally the intermediate compounds, to follow the changes in the oxidation states of metals in the course of the catalytic process, and to give a quantum-chemical description of substrate coupling with the metal [1,2].

As well as the fundamental significance of MCC in the formation of basic ideas regarding catalysis as a whole, the practical advantages MCC can

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0010-8545/90/$13.65

provide are of great importance. These advantages are the comparatively mild conditions under which the reaction can be conducted in solution (low temperatures and pressures), a low sensitivity to impurities and catalytic poisons, a high availability of active centres for interaction with the substrate, and the possibility of exercising control over the catalytic system by varying the ligand environment and the composition of the medium. The much more readily available homogeneous catalysts are, in a number of cases, superior to heterogeneous catalysts in their selectivity.

The principles of MCC can be easily transferred to the catalysis of electrochemical reactions. For instance, metalloporphyrins were successfully used in the electrocatalytic reduction of oxygen in fuel cells, with the aim of replacing precious metals or substantially reducing their consumption [3]. Of greatest interest, however, is the very recent use of MCC in electrosynthesis. Several factors may be noted which make a combination of MCC with electrochemistry especially attractive to specialists working in different fields. There is primarily the possibility for the electrode to replace strong oxidants and reductants, which are often expensive and difficult to obtain, and, moreover, pollute the reaction mixture with the products of their transformation. Conducting the redox reaction on the electrode makes it possible to influence the reaction rate within wide limits by varying the electrode potential and to transfer any number of electrons without changing the composition of the medium. This is especially important in multielectron reactions. Finally, it should be particularly noted that MCC can effect electrochemical reactions which are impossible in the absence of metal complexes, e.g. the reduction of nitrogen or CO. It should be added that such modern methods for investigating electrode processes as different kinds of polarography, cyclic voltammetry, and various pulsed methods, combined with electrolysis under the conditions of controlled potential and spectral methods, when applied together, make it possible to describe in sufficient detail the mechanism of the catalytic process.

In summing up the aforesaid it may be noted that the words of a well-known electrochemist M. Baizer are fully applicable to metal complex electrocatalysis (MCE): "Unlimited opportunities await the investigator who intends to work at the junction of organic chemistry, electrochemistry and catalysis. At his disposal are the 'pure' methods of electron insertion and removal; the methods of applying potential catalysts onto electrode matrices; the advantages of adsorption on electrodes, which depends on the electric field; a large set of solvents; and, if necessary, background electrolytes, influencing in a specific manner the electrode processes and the behaviour of intermediate particles in solution" [4].

The recent ever-increasing amount of work devoted to the use of metal complexes in electrocatalysis calls for a systematic study of the data accumulated in this virtually new field of chemistry. It is necessary to understand the methodology of selecting metal complex catalysts for electrochemical reactions, the general principles of their function, the possibilities and prospects of their use in the electrochemical conversion reactions of various substrates. These questions are examined in the present paper.

B. GENERAL PRINCIPLES

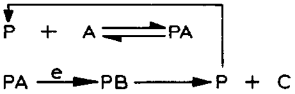
Metal complex electrocatalysts can be subdivided into two main groups according to the mechanism of their action. The first group includes the metal complexes whose coordination sphere remains invariable in the course of the whole catalytic cycle, and the electron transfer takes place via an outer sphere mechanism without the formation of an intermediate complex between the substrate (A) and the catalyst (redox couple P/Q):

$$P + e \rightleftharpoons Q$$

$$Q + A \rightleftharpoons P + B \longrightarrow C$$

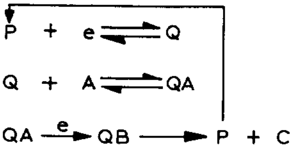
It has been suggested that this type of MCE should be designated as redox catalysis [5]. The function of a redox catalyst (mediator) is to transfer the electron from the electrode to the substrate, after which the primary product of substrate reduction, B, is converted into the final product C in the course of a chemical reaction. In the case of a rapid and irreversible conversion of B into C the substrate may be reduced under the conditions of a homogeneous electron transfer against the standard potential drop ($E^\circ_{P/Q} > E^\circ_{A/B}$) [6], which considerably expands the possibilities of redox catalysis. An obvious gain from the use of redox catalysts will only be obtained in the case where they are capable of being rapidly regenerated on the electrodes with a high current yield at potentials more positive than those of the substrate direct electroreduction, or less positive than those of its direct electro-oxidation, and when these catalysts are stable and can interact rapidly with the substrate. It is thus expedient to apply this kind of MCE when a change-over to homogeneous electron transfer increases the rate of the process as a whole, owing to the reaction being transferred to the bulk of the solution when there is a decrease in the overpotential of the electrochemical reaction, as well as in the case of such substrates for which homogeneous redox reactions proceed, for some reason or other, at higher rates than the heterogeneous reactions.

The second group of catalysts contains metal complexes where electron transfer from the electrode to the substrate takes place via an inner mechanism, with the formation of an intermediate complex between the catalyst and the substrate (PA or QA). In a simplified way the mechanism of the action of these catalysts can be represented by the following catalytic schemes:



Scheme 1.

or



Scheme 2.

The catalytic cycle involves the transformation of the substrate in the coordination sphere of the metal complex; it is therefore appropriate to define this kind of MCE as coordination electrocatalysis. The coupling of the electrochemical stage and the chemical reaction of the substrate takes place with the participation of the catalyst–substrate complex as a whole, and the function of the catalyst is to bind and activate the substrate in the metal complex coordination sphere, as a result of which the reactivity of the substrate in the electron exchange reaction with the electrode increases. As distinct from redox catalysis, P or Q in coordination MCE must be coordinatively unsaturated or contain ligands that are kinetically labile in substitution reactions. This is necessary for the formation of the intermediate complexes PA and QA.

The choice of a particular metal complex for coordination MCE is simplified considerably by the availability of a large amount of data regarding the complexation and activation of substrates which are kinetically inert in redox reactions. These can be found in numerous monographs on MCC and the chemistry of coordination and organometallic compounds [1,2]. After having chosen the appropriate metal complex binding the substrate and activating it in the metal complex coordination sphere, one can begin to solve the practical questions of coupling the electrode and the chemical reactions of substrate conversion. This strategy is obviously idealized, but the correctness of this approach will be illustrated below by a number of examples.

In coordination MCE the metal complex can be immobilized on the electrode surface, for example, as a result of adsorption or special fixation techniques [7], or be present in the bulk of the solution. Electron exchange between the electrode and the catalyst–substrate complex can in this case be realized either directly or via redox mediators. In particular, if the reaction centre in the immobilized catalyst exchanges its electrons with the electrode slowly, the efficiency of this exchange can be enhanced by immobilizing on the electrode surface a redox mediator capable of fast electron exchange both with the electrode and the reaction centre. It will be shown that this approach, developed in bioelectrocatalysis for the coupling of the enzymatic and the electrochemical reactions [8], can also be successfully applied in coordination MCE.

In conclusion, coordination MCE is in fact the only method of drawing into electrochemical reactions a substrate whose direct reduction–oxidation on the electrode is hampered or does not occur at all. In the present review, attention is therefore given mainly to this kind of MCE.

C. THE PRINCIPAL ELECTROCHEMICAL REACTIONS CATALYSED BY METAL COMPLEXES

(i) Dehalogenation of organic halides

The problem of the dehalogenation of organic halides RX (where R = aryl, alkyl; X = Cl, Br, I) is not only of theoretical but also of practical importance, since numerous halides accumulate in the wastes of industrial organic syntheses. Direct electroreduction of alkyl and aryl halides is mostly performed at potentials which are more negative than -2 V [4]. (All the potentials in the review are given relative to the aqueous saturated calomel electrode.) The picture changes radically when complexes of certain transition metals, capable of reacting with RX and forming more readily reducible compounds, are introduced into the electrolyte solution. The reductive dehalogenation of RX can in this case be conducted at considerably more positive potentials, most often at those of the regeneration of the metal complex active with respect to RX.

The complexes which are catalytically active with respect to RX can be tentatively subdivided into three groups: phosphine, tetraazamacrocyclic and polypyridyl complexes. Let us now consider each one of these groups.

Tetraphosphine complexes of zero-valent nickel, NiP_4, electrically generated by the two-electron reduction of Ni^{2+} or NiX_2P_2 in the presence of an excess of phosphine (P), catalyse the electroreduction of RX (R = alkyl, benzyl) and ArX (Ar = aryl), producing a mixture of the corresponding hydrocarbons (RH or ArH), the products of coupling (R–R or Ar–Ar), and, in the case of alkyl halides, R($-$H) alkenes as well [9–11]. The reduction is performed at mercury, platinum, gold or glassy-carbon cathodes in a diaphragm cell in various solvents (EtOH, tetrahydrofuran (THF), MeCN etc.). The ratio of the products depends essentially on the nature of the solvent but not on the nature of the electrode. Thus, in the catalytic electroreduction of ArX in an alcoholic medium the only product is the corresponding ArH, whereas in THF or in its mixtures with hexamethylphosphoramide (HMPA) it is a mixture of ArH and Ar–Ar, with the yield of diaryl rising to 70–95% with increasing HMPA content in the mixture [9]. On the basis of an electroanalytical study of this reaction, the mechanism of the formation of dehalogenation products can be illustrated by a scheme for aryl halides [9]:

$$\mathrm{Ni^{2+}} \xrightarrow{2e^-,\,P} \mathrm{NiP_4} \xrightarrow{\mathrm{ArX}} \mathrm{ArNiXP_2} \xrightarrow{2e^-,\,H^+} \mathrm{Ar^-} + \mathrm{NiP_4}$$

$$\mathrm{Ar^-} \xrightarrow{H^+} \mathrm{ArH}$$

$$\mathrm{Ar^-} + \mathrm{ArNiXP_2} \longrightarrow \mathrm{Ar{-}Ar} + \mathrm{X^-} + \mathrm{NiP_4}$$

For alkyl halides the intermediate formation of a σ-organonickel derivative $RNiXP_2$ is also assumed, resulting from the reaction of the oxidative addition of RX to NiP_4, whose stability and subsequent transformation routes depend essentially on the nature of the solvent and the halide [10]. The phosphines used are tributylphosphine [10], triphenylphosphine [9,10] and diphosphines of the bis(diphenylphosphino)ethane (dppe) type [12].

A study of the mechanism of electroreduction at the mercury cathode of such RX compounds as 1-iodobutane, 1-iodo-2,2-dimethylpropane, benzyl chloride and PhBr in an MeCN medium in the presence of catalytic quantities of $[Ni(PPh_3)_2(MeCN)_4]^{2+}$ and an excess of PPh_3 concluded that the electrochemically generated $Ni(PPh_3)_4$ is also an active species with respect to RX [13]. The further conversion of $RNiX(PPh_3)_2$ (I), formed as a result of the oxidative addition reaction, depends on the nature of the organic halide and proceeds according to one of the following possible schemes:

$$\mathbf{I} \xrightarrow{e^-} [\mathrm{RNi(PPh_3)_2X}]^- \longrightarrow \mathrm{R{-}R} + \mathrm{Ni(PPh_3)_4} + \mathrm{X^-}$$

$$\mathbf{I} \longrightarrow \mathrm{Ni(PPh_3)_3X} + \mathrm{R^{\cdot}} \longrightarrow \mathrm{R{-}R} + \mathrm{RH} + \mathrm{R(-H)}$$

or via a hydride complex

$$\mathbf{I} \longrightarrow \mathrm{R(-H)} + [\mathrm{Ni(PPh_3)_2(H)X}] \longrightarrow \mathrm{Ni(PPh_3)_3X} + \mathrm{RH} + \mathrm{H_2}$$

followed by the electrochemical regeneration of $Ni(PPh_3)_4$. The same complex can act as the promoter of the electroreduction of allyl halides in MeCN medium to 1,5-hexadiene with a current yield of 85–95% [14]. A nickel(I) π-complex of composition $(\pi\text{-}C_3H_5)Ni(PPh_3)Cl$ is assumed to be formed as an intermediate in the oxidative addition of the substrate to $Ni(PPh_3)_4$. The subsequent one-electron reduction of this intermediate is accompanied by cleavage of the C–Ni bond with the regeneration of the catalyst and the formation of X^- and with the $C_3H_5^{\cdot}$ radical undergoing dimerization with the formation of hexadiene. Essential in this electrocatalytic reaction is a tenfold excess of PPh_3 with respect to Ni^{2+} which is the initial ion yielding $Ni(PPh_3)_4$.

Together with the diphosphine complexes of nickel, the product of reversible one-electron reduction, $[Rh(dppe)_2]^+$, also manifests its catalytic activity in the dehalogenation reaction [15]. In the absence of the substrate, $Rh(dppe)_2$, electrochemically generated at the mercury cathode, reacts with the solvent (dimethyl sulphoxide (DMSO), MeCN etc.), forming the $RhH(dppe)_2$ hydride; in the presence of cyclohexyl chloride a mixture of cyclohexane and cyclohexene is formed. The fact that dicyclohexylmercury was found as a side product is indicative of the reaction proceeding via intermediate formation of a free cyclohexyl radical.

Ni(0)–phosphine complexes can be also used to introduce RX into more complex reactions. For instance, in ref. 16 it was shown that in an *N*-methylpyrrolidone medium or in a THF–HMPA mixture (gold cathode) the complex $[NiP_2EX]^-$ ($X = Cl, Br, I$), generated by Ni^{2+} reduction in the presence of a threefold excess of triphenylphosphine ($P = PPh_3$) and alkene (E = ethylene, propylene, styrene), reacts with benzene halides (PhX, where X = Cl, Br, I) with the formation of the corresponding arylalkenes according to the following scheme (e.g. when $E = C_2H_4$):

$$NiP_2X_2 + E \xrightarrow{2e^-} NiP_2EX^- \xrightleftharpoons{PhX} \text{“PhNiX”} \xrightarrow{Et_3N} PhCH{=}CH_2 + Ni(0) + Et_3NHX$$

The olefin arylation reaction results from the reversible oxidative addition of PhX with the formation of an organonickel complex “PhNiX” of unknown structure, which decomposes irreversibly with the formation of an arylalkene. The process becomes catalytic only in the presence of a base (Et_3N) which seems to promote the elimination of HX.

Another example of RX involvement in the synthesis of more complex products is described in ref. 17, where the electrocatalytic synthesis of arylacetic and arylpropionic acids is shown to be possible. These acids are formed as a result of the electroreduction of the corresponding benzyl halides at a mercury cathode in CO_2-saturated aprotic media (mixtures of THF with HMPA or *N*-methylpyrrolidone) in the presence of catalytic quantities (10%) of Ni(0)–diphosphine or Pd(0)–diphosphine complexes in solution. The products are formed in accordance with the scheme proposed below (D = diphosphine):

$$MD_2 \xrightarrow[-D]{RX} RMXD \xrightarrow[-X^-]{2e^-} RMD^- \xrightarrow{CO_2,\, D} RCO_2^- + MD_2$$

The yield of the acids amounts to 20–50% with the formation of dibenzyls as side products.

Another group of complexes catalysing the electroreduction of RX consists of square-planar nickel(II) and cobalt(II) complexes with tetraazomacrocycles (L) or Schiff bases. In ref. 18, for instance, complexes of composition NiL^{2+} in aprotic media (MeCN, dimethylformamide (DMF), DMSO etc.) were shown to undergo one-electron reduction to stable NiL^+, which enters into oxidative addition reactions with RX (2-bromooctane, 2-bromo-2-methylheptane etc.), forming organonickel $[RNi(L)Br]^+$ compounds (**II**) whose further fate depends on the nature of R. In the case of primary RBr the dehalogenation products (RH, R(−H) and R–R) are formed as a result of competing reactions (**II** + RBr → R–R and **II** $\xrightarrow{e^-}$ R^- $\xrightarrow{H^+}$ RH), whereas secondary and tertiary RBr are dehalogenated exclusively via a radical mechanism (**II** → $R^{\bullet}$ → RH, R(−H), R–R) [18]. The dehalogenation reaction is catalytic and takes place at potentials corresponding to $E°(NiL^{2+/+})$. It is of interest to note that insertion of any substituents into L shifts $E°(NiL^{2+/+})$ to the anodic region, with the maximum effect being produced by substituents at the nitrogen atoms of the ligand, which makes it possible to lower RBr reduction potentials to −1 V [18]. The main products of the dehalogenation of RBr in the presence of nickel(II) complexes with Schiff bases are the corresponding R–R dimers, which indicates that the reaction proceeds mainly via a radical mechanism [19].

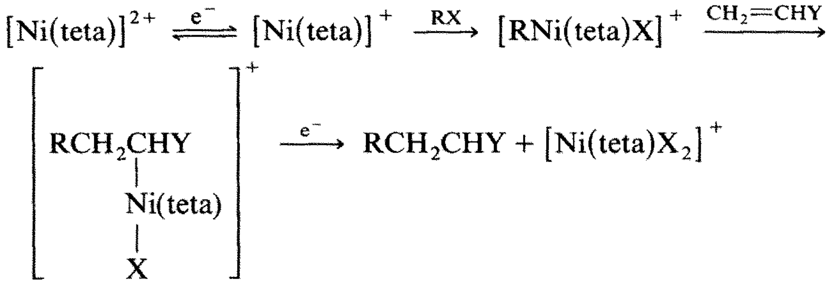
Similar catalytic activity is displayed in the reaction of RX dehalogenation with tetraazamacrocyclic complexes CoL^{2+} [20,21] and cobalt(II) complexes with Schiff bases [22] at cobalt(II/I) redox-transition potentials. For instance, in the dehalogenation of BuX (X = Cl, Br) in the presence of electrochemically generated bis(salicyclideneiminato)cobalt(I), $[Co(salen)]^-$, the main product is 2-methylpropene. The fact that alkylcobaloxime [BuCo(salen)] is formed as the side product is indicative, in the authors' opinion [22], that the reaction proceeds via the intermediate formation of a butyl radical.

Formation of alkylcobaloximes [RCo(salen)] in the reaction of $[Co(salen)]^-$ with RX was used as described in ref. 23 for the electrocatalytic carboxylation of organic halides. The electrolysis of allyl and benzyl halides ($R = PhCH_2$, $Ph(CH_3)CH$, $PhCH{=}CHCH_2$, $CH_3CH{=}CHCH_2$ etc.; X = Cl) at the mercury cathode in a THF–HMPA mixture, CO_2 saturated under atmospheric pressure, in the presence of [Co(salen)] catalyst results in the formation, after hydrolysis of a catholyte, of the carboxylic acids RCO_2H with yields of 50–97%. In a moist solvent (H_2O content $(1-5) \times 10^{-2}$ M) the yield of the acids is reduced, with the simultaneous appearance of the corresponding RH and R–R in the products. No formation of acids is observed in the case of aliphatic halides (bromopropane) or bromostyrene, and from aryl halides the acids are formed after the replacement of [Co(salen] with $Ni(Ph_3P)_4$. The formation of acids is assumed to be described by the following scheme:

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

The reaction proceeds either via the intermediate formation of a CO_2 adduct with alkylcobaloximes or by CO_2 being attacked by the carbonium ion formed upon [RCo(salen)] dissociation. In the light of these data it is appropriate to mention the work [24] where two-electron stage-by-stage reduction of alkylcobaloximes [RCo(dmg)Py] (where R = alkyl, benzyls; dmg = dimethyl glyoximate; Py = pyridine) was shown to be accompanied by the formation of a dealkylated cobalt(I) complex, whose two-electron reoxidation regenerates the initial alkylcobaloxime in 60–95% yield. For optically active groups R, the reduction–oxidation of the initial complex is accompanied by a complete inversion of configuration. On the basis of the data obtained in ref. 24, a mechanism for the Co–R bond cleavage in the reduction of alkylcobaloximes was proposed. According to this mechanism the axial group R splits off in the form of $R^{\cdot}$ or R^-, which remains reversibly bound with the cobalt(II) or cobalt(I) complex as a result of its transfer to the nitrogen atom of the equatorial dmg ligand. It is quite possible that in the course of the synthesis of carboxylic acids [23] the reduction of [RCo(salen)] is also accompanied by R being transferred to the axial ligand, with a coordination site becoming simultaneously available for the CO_2 molecule. After the coordination and activation of CO_2, R is again transferred, but now to the CO_2 molecule, with the formation of carboxylate ion.

The complexes structurally modelling vitamin B_{12} can most probably also be used to draw alkyl halides into other interesting reactions, e.g. reductive cross-coupling. For instance, by the electrolysis of a mixture of ethyl iodide and acrylonitrile in MeCN at a carbon electrode polymer-modified with vitamin B_{12} 3,5-diaminobenzoyl derivative, valeronitrile is selectively obtained [25]. The $[Ni(teta)]^{2+}$ (teta = hexamethyltetraazacyclotetradecane) complex catalyses the electrochemical dehalogenation reaction of RX (e.g. 1-bromooctane) with the formation of RH (30%), R–R (45%) and R(–H) (20%) [26,27]. Upon additional introduction, along with RX, of activated olefins ($CH_2{=}CHY$, where Y = Ar, CN, CO_2Et etc.) into the catholyte, the RCH_2CH_2Y products of cross-coupling are observed to form. This reaction is not catalytic because the $[Ni(teta)X_2]^+$ complex formed in accordance with the scheme below is electrochemically inactive [26]:



$$[\mathrm{Ni(teta)}]^{2+} \overset{e^-}{\rightleftharpoons} [\mathrm{Ni(teta)}]^{+} \xrightarrow{\mathrm{RX}} [\mathrm{RNi(teta)X}]^{+} \xrightarrow{\mathrm{CH_2{=}CHY}}$$

$$\left[\begin{array}{l} \mathrm{RCH_2CHY} \\ \qquad | \\ \qquad \mathrm{Ni(teta)} \\ \qquad | \\ \qquad \mathrm{X} \end{array}\right]^{+} \xrightarrow{e^-} \mathrm{RCH_2CHY} + [\mathrm{Ni(teta)X_2}]^{+}$$

The third group of complexes catalysing the reductive dehalogenation of RX includes the polypyridyl complexes of the metals of group VIII. In refs. 28 and 29, $\mathrm{Co(bpy)_3^{2+}}$ (bpy = 2,2′-dipyridyl) in MeCN was shown to catalyse the reductive dimerization of allyl halides to 1,5-hexadiene. Hexadiene is formed at $\mathrm{Co(bpy)_3^{2+/+}}$ redox-transition potentials, i.e. at potentials 1.2 V more positive than for the reduction of allyl chloride itself at a platinum electrode [29]. Along with hexadiene, $-[\mathrm{CH_2CH(CH_2Cl)}]_n-$ oligomers are formed. The same reaction can also be carried out in an aqueous medium, using sodium dodecylsulphate for allyl chloride solubilization [30].

Hexadiene formation is also observed in the electroreduction of allyl bromide in MeCN in the presence of $\mathrm{Ni(bpy)_3^{2+}}$ and a tenfold excess of the ligand [31]. Two-electron reduction of $\mathrm{Ni(bpy)_3^{2+}}$ is assumed to be accompanied by detachment of the ligand, and the $\mathrm{Ni(bpy)_2}$ formed in situ enters into the oxidative addition reaction with allyl bromide, forming a π-bonded organometallic derivative of monovalent nickel, π-$\mathrm{C_3H_5Ni(bpy)Br}$. The latter is converted into the end product by a chemical (with $\mathrm{Ni(bpy)_3^{2+}}$ regeneration) or an electrochemical (with $\mathrm{Ni(bpy)_2^{0}}$ regeneration) mechanism.

Alkyl and aryl bromides are dehalogenated mainly with the formation of R–R dimers in DMF in the presence of $\mathrm{Ni(phen)_3^{2+}}$ (phen = 1,10-phenanthroline) as the catalyst [32].

Alkyl and aryl halides can be electrochemically dehalogenated at a cathode pre-modified with the products of the reduction of metal complexes. For instance, 1-bromooctane is dehalogenated in DMF in a diaphragmless cell with aluminium electrodes, one of which (the cathode) is covered with an iron-containing deposit formed as a result of the previous electroreduction of $\mathrm{Fe(acac)_3}$ (acac = acetylacetonate). RBr dehalogenation in this case takes place at potentials 0.9 V more positive than at the aluminium cathode [33]. Under similar conditions the cathode covered with the deposit formed in $\mathrm{Ni(acac)_3}$ electroreduction catalyses the dehalogenation of aryl and benzyl halides [34].

1,1-Dibromo-2-phenylcyclopropane is dehalogenated with the formation of 1-bromo-2-phenylcyclopropane (90%) and phenylallene (10%) in the presence of catalytic quantities of $\mathrm{CrCl_3}$. The reduction is performed at a lead cathode in DMF at $Cr^{3+/2}$ redox-transition potentials, which are more than 2 V more positive than the potentials of the electroreduction of the halide itself [35].

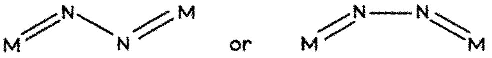
Examples of other electrodehalogenation reactions of organic halides, catalysed by metal complexes, can be found in a review [36].

On the whole, the electrocatalytic dehalogenation of organic halides appears to be a promising area of metal complex electrocatalysis, both in fundamental research and in all probability in its practical applications, in particular for the treatment of effluents containing toxic organic halides.

(ii) Reduction of molecular nitrogen and of organic compounds with multiple bonds

The problem of mild nitrogen fixation has attracted the close attention of investigators in the last 20 years. Although the biological fixation of nitrogen has been known for a long time, the mechanism of this highly important reaction remained unknown until recently. Attempts to find simple chemical reactions that would make it possible to reduce nitrogen to NH_3 under the conditions similar to those of biological fixation have repeatedly been made. However, they encountered difficulties associated with the rupture of the exceptionally strong triple bond in nitrogen (920 kJ mol^{-1}).

Theoretical consideration [37] showed that the most economical reaction path (in the sense of energy expenditure) in protic media includes nitrogen activation in a linear binuclear complex $M \cdots N{\equiv}N \cdots M$. This leads to a considerable weakening of the bond between the nitrogen atoms, and the best catalytic properties could be expected for ions of metals with the d^3 (Mo^{3+} and V^{2+}) electronic configuration. The multielectron reduction of nitrogen to N_2H_4 and NH_3 can proceed in this case without the intermediate formation of the thermodynamically extremely unfavourable diimide N_2H_2 under the conditions of a more uniform energy distribution over the individual stages. Such equalization of the energy pattern is achieved owing to the stabilization of the intermediates formed as a result of the "conjugation" effects, i.e. the overlapping of metal d-orbitals and nitrogen p-orbitals, for example, in hydrazine derivatives with a planar configuration:



From the viewpoint of metal complex electrocatalysis a possible approach to creating an electrocatalyst should include a search for an appropriate $M(d^3)$ complex capable of activating nitrogen by the coordination mechanism described above and reacting either directly on the electrode or with the participation of the appropriate mediator.

The first attempts at creating electrochemical systems for nitrogen reduction were based on the $Ti(OH)_3$–Mo(III) nitrogen-fixing hydroxide system in alkaline methanolic solution, where molybdenum(III) acted as nitrogen-activating catalyst and titanium(III) as the reductant [38]. The data on the participation of a large number of titanium(III) ions in electron transfer to the active centre [28] suggested the possibility that titanium(III) could be used as mediator in amalgam or electrochemical reduction. Indeed, the introduction of sodium amalgam into this system made it possible to raise considerably the yield of N_2H_4 and NH_3 [39,40], with the formation of nitrogen-fixation products already observed at 20 ° C, whereas in the absence of the amalgam the reaction was conducted at temperatures above 80 ° C. The relatively slow N_2H_4 reduction in this system and a study of NH_3 accumulation kinetics indicated that the nitrogen-fixation products were formed in parallel reactions [40].

The results obtained in the amalgam reduction of nitrogen led to the direct electrochemical reduction of nitrogen on a mercury cathode in the same system [41]. The maximum yield of N_2H_4 and NH_3 in this case proved to be attained at the current density of 0.5 mA cm^{-2} or the potential of -1.86 V, i.e. under the conditions of sodium amalgam formation on the electrode [42]. In the region of more positive potentials the reaction rate, in accordance with the slow-discharge theory, decreased exponentially with the drop in the absolute value of the potential, and at more negative potentials the adsorption of charged hydroxide species was hindered. When the mercury cathode is replaced with a rotating copper amalgamated electrode (3000 rev min^{-1}) the nitrogen electroreduction reaction becomes N_2H_4 selective. In ref. 43 this was explained by the short time of contact between the catalyst particles and the electrode surface, because of which the transfer of six electrons with the formation of NH_3 became less probable than the four-electron reduction of nitrogen to N_2H_4.

A study of the electrochemical behaviour of titanium(III) and titanium(IV) chlorides in methanol made it possible to find the conditions under which the solution remained homogeneous even at a relatively high alkalinity (guanidine buffer, pK_α 13.6) and titanium(IV) was reduced to titanium(III) [44]. The addition of molybdenum(III) did not disturb the homogeneity of the solution. The N_2H_4 formation, catalysed by this system, in the electrolysis in a diaphragm cell (mercury pool cathode, nitrogen pressure of 30 atm) started at -1.6 V, which corresponded to the half-wave potential of the reduction $Ti(IV) + e \rightarrow Ti(III)$. The reaction rate was radically influenced by the composition of the medium [45,46]. An increase in alkali concentration in the system as a result of hydrogen evolution at the cathode led to a decrease in the N_2H_4 formation rate, which, however, increased again to its previous value upon the addition of water. It was assumed that heteronuclear titanium(III) and molybdenum(III) complexes were the active species in nitrogen reduction, and that the titanium(III) complexes could act as electron carriers. The catalytic system with components in the Ti : Mo molar ratio of 3 : 1 preserved its activity in the course of electrolysis during more than 14 h.

Similar results were obtained in the amalgam reduction of nitrogen in the Ti(III)–Mo(III)–catechol (H_2cat) system in aqueous media [47]. Catechol forms complexes with titanium ions. These complexes are stable in aqueous media over a wide range of pH (pH 5–13) and react reversibly on the electrode:

$$\mathrm{Ti(cat)_3^{2-}} + e^- \rightleftharpoons \mathrm{Ti(cat)_3^{3-}} \qquad E^\circ = -1.4\ \mathrm{V}$$

Molybdenum ions also form soluble complexes with catechol; their composition depends on the pH of the medium and the method of preparation [48,49]. The most active nitrogen-fixation system can be obtained on reduction of the initial solution of $Ti_2(SO_4)_3$ and Na_2MoO_4 with a gradual increase in alkalinity of the solution from pH 3–4 to pH 7 as a result of hydrogen evolution in the course of electrolysis. Under these conditions, according to polarographic data, the $\mathrm{Mo(VI)} + e \rightarrow \mathrm{Mo(V)}$ reduction is accompanied by the $2\mathrm{Mo(V)} \rightarrow (\mathrm{Mo(V)})_2$ dimerization. Binuclear catechol complexes of $(\mathrm{Mo(V)})_2$ are irreversibly reduced under electrolysis, most probably forming polynuclear molybdenum(III) complexes. The yield of N_2H_4 and NH_3 in the Ti(III)–Mo(III)–catechol system passes through a maximum at the Ti : Mo ratio of 6 : 1. Without titanium(III), as was the case in all the above systems, molybdenum(III) exhibited a very weak catalytic effect, with the formation of N_2H_4 and NH_3 in trace quantities.

The possibility of nitrogen electroreduction in aqueous media in the presence of molybdenum complexes was first noted in ref. 50. However, these data, as well as the data on the amalgam nitrogen reduction in methanol solutions, catalysed by molybdenum carbonyl complexes [51], were poorly reproducible, although the very fact of N_2H_4 formation was beyond doubt. In ref. 52 the authors succeeded in obtaining reproducible results, using as a catalyst the molybdenum(III) complexes produced by the reduction of molybdenum(V) in alkaline methanol solutions in the presence of magnesium ions. An electrochemical [53–55] and a kinetic [53,56] study of this system showed the species which were active with respect to nitrogen to be composed of molybdenum(III) and magnesium. The catalytic complex was functioning in an absorbed state on the amalgam surface; the catalyst, however, was deactivated fairly soon in the course of the reaction. The only nitrogen reduction product in this system was N_2H_4. These results served as the basis for a search for molybdenum(III) complexes capable of being strongly adsorbed on the amalgam surface owing to the surface activity of the ligand. After testing a large number of surfactants of a different nature the authors [57] observed a considerable and well-reproducible increase in the catalytic activity of molybdenum(III) in the presence of dipalmitoylphosphatidylcholine (DPPC) [57]. A characteristic feature of the structure of this molecule, which belongs to the class of phospholipids, is a combination of hydrophobic "tails", palmitic acid residues, and a bipolar "head" including a negatively charged phosphate group and a positively charged quaternary ammonium group. As follows from capacitance measurements [58,59], DPPC forms an adsorption layer on the negatively charged surface of the mercury electrode, orienting itself vertically with the "head" towards the surface and the hydrophobic "tails" towards the solution. The active species are assumed [56] to be the binuclear $(Mo(III))_2$ complex stabilized as a result of the interaction with phosphate (or carbonyl) groups of adsorbed DPPC. The same activation energy (about 36 kJ mol^{-1}) for N_2H_4 and NH_3 formation shows that in the parallel reactions in which these products are formed there is a common limiting stage. This stage can consist of electron transfer from the amalgam to the active complex with the formation of a molybdenum derivative of hydrazine (N_2^{4-}). This process is facilitated by a simultaneous transfer of protons from the solvent through the hydrophobic DPPC layer and formation of the $N_2H_n^{(4-n)-}$ fragment. At nitrogen pressures above 50 atm, when the rate of N_2H_4 and NH_3 formation ceases to depend on the pressure, the yield of products calculated according to the sodium content in the amalgam is approximately 2%.

A further improvement in this catalytic system was attained as a result of introducing tertiary phosphines, in whose presence a significant catalytic effect was already observed at the atmospheric pressure of nitrogen [60]. The cocatalytic effect of phosphines was only reached in the presence of the phospholipid, and their joint (synergistic) action led to the rate being increased 10^3-fold compared with the rate of the reaction without the phospholipid. Under these conditions the reaction rate practically coincided with the rate of the biological fixation of nitrogen (0.1–1 N_2 molecule per second per active centre). At 50 atm nitrogen pressure the concentration of N_2H_4 reached 2.6×10^{-2} mol l^{-1}, and the overall yield of the reductant amounted to 20%.

Recently nitrogen fixation in the Mo(III)–DPPC–phosphine system has also been successfully achieved during electrolysis on a mercury cathode [61].

Although the structure of this multicomponent system, which is the most active of all those known, is still not clear in detail, its investigation by the cyclic and the alternating current voltammetry techniques [54,55,62] has thrown some light on the functions of its individual components. For instance, in ref. 62 the adsorption layer was assumed to include two kinds of molybdenum(III) complex, one of which contains only the molybdenum, binds and activates nitrogen (the active site), but exchanges its electrons with the electrode slowly. The second complex, of composition Mo–Mg, does not activate nitrogen, but exchanges its electrons with the electrode and the active site rapidly and reversibly and can thus perform the functions of a redox mediator necessary for the coupling of the electrochemical and the chemical stages of the catalytic process. Because of the stronger adsorptive properties of the mediator its concentration on the amalgam surface is substantially greater than that of the active site. The phospholipid, being coordinated with the active site, raises its adsorbability and approximately equalizes the surface concentrations of both components, maintaining them in the ratio optimal for the effective functioning of the catalytic system. This, as already noted, is aided by the strong adsorption of the phospholipid owing to the charge of its polar "head". The incorporation of the active site into the lipid film specifies a quite definite spatial location of the active centre relative to the surface of the electrode or the amalgam, and also prevents catalyst deactivation in the course of the reaction, as observed earlier in a system without the phospholipid [53]. Coordination with phosphines enhances the electron-acceptor properties of the mediator (and possibly of the active site), which must raise the rate of electron transfer from the amalgam onto the substrate. On the whole, creation of a spatially ordered structure, active site–mediator–external source of electrons (the amalgam or the electrode), lowers the energy barrier of electron transfer onto the coordinated nitrogen molecule, which results in a catalytic effect comparable with the rates of enzymatic nitrogen fixation.

Other metal complexes catalysing nitrogen electroreduction in protic media (water, THF–CH_3OH mixture) include the $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ clusters [63]. Electrolysis for 24 h in the presence of these complexes at $E = -1.7$ V and 20 °C under an atmospheric pressure of nitrogen leads to the formation of NH_3 with a 1.6% current yield.

One can also mention studies on the reduction of nitrogen to NH_3 in hydrochloric acid solutions in the presence of molybdenum and zinc chloride complexes [64] and direct nitrogen reduction on an iron cathode in alkaline solutions [65] with an NH_3 current yield not exceeding 1%. The detection of small quantities of NH_3 has to be thoroughly controlled by means of parallel experiments with an inert gas or $^{15}N_2$. Without such control, erroneous conclusions on nitrogen reduction in a particular system may be drawn. The extent to which such an error is possible is demonstrated in ref. 66, where after repeated tests in an inert gas atmosphere it was shown that the NH_3 detected in the electrochemical and photoelectrochemical nitrogen reduction on iron or semiconductor GaP cathodes is formed owing to the reduction of nitrate and nitrite impurities in the reagents used. Therefore in refs. 64 and 65, where such a test was not carried out, the occurrence of nitrogen reduction is doubtful.

From a general evaluation of the studies on the electrochemical reduction of nitrogen in protic media it is evident that they are of great theoretical interest and lay the foundation for future technologies of NH_3 and N_2H_4 production under mild conditions. However, these studies have not yet gone beyond the stage of purely laboratory methods.

The systems discovered in 1964 by Volpin and Shur [67] formed the basis for the development of electrochemical systems making possible nitrogen reduction in aprotic media. These systems included a strong chemical reductant (organomagnesium, organolithium, organoaluminium compounds, lithium aluminium hydride, metallic magnesium) and a transition metal compound capable of forming a complex with molecular nitrogen. The final products of nitrogen reduction in these systems are compounds of the nitride type, the hydrolysis of which leads to NH_3. In these systems in the presence of aprotic Lewis acids the yield of bound nitrogen exceeded by factors of tens and hundreds the amount of catalyst used.

In ref. 68 a number of electrocatalytic systems were proposed. In the most effective system, about 3 mol of NH_3 were formed per 1 mol of titanium compound in the electrolysis of a solution of naphthalene, titanium and aluminium isopropoxides in dimethoxyethane using an aluminium anode and a nichrome cathode and with nitrogen blown through the cell. The reaction mechanism was not studied, but naphthalene was assumed to play the role of the redox mediator, aluminium isopropoxide that of the Lewis acid, with titanium(II) alkoxy derivatives serving as the catalyst.

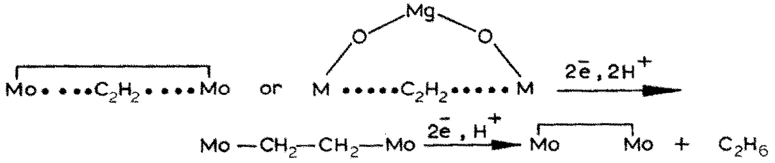
A fundamentally different approach to direct production of organonitrogen compounds, in particular, aromatic amines, from molecular nitrogen was developed by Volpin and Shur [67]. It consists of the insertion of nitrogen into the metal–aryl bond or of the direct nucleophilic attack on the nitrogen ligand by the carbanion, followed by the reduction of the metal-coordinated ArN=N group. As a result of the further development of research on the alkylation and acylation of the nitrogen ligand, stable diazoalkane, diazenide and hydrazide derivatives were obtained, from which free amines can be isolated by various destructive methods [69].

In refs. 70 and 71 it was shown that destructive methods of isolating substituted hydrazines and amines from molybdenum and tungsten hydrazido and diazenido complexes can be replaced by the electroreduction of these complexes on mercury or platinum cathodes in an aprotic medium, using the traces of water in the solvent as the source of protons. This produced *N*-aminopiperidine [70] and 5-amino-4-cyanopyrazole [71] with yields of 60–70%. Despite the attractiveness of this approach, the problem of creating a continuous catalytic cycle for producing amines from molecular nitrogen is still far from solved. The main difficulties to be overcome are associated with a considerable contribution of side reactions, the regeneration of the initial complexes and the isolation of the desired products from the reaction mixture without destroying the catalytic system.

Among compounds with multiple bonds, the reduction of which is catalysed by molybdenum(III) complexes, acetylene (C_2H_2) is the most convenient substrate for the study of the kinetics and the mechanism of the electrocatalytic reaction, since the hydrocarbons formed here are easy to analyse by gas chromatography and the product distribution is highly sensitive to the structure of the catalytically active species. In refs. 72 and 73, Mo(III)–cysteine complexes in aqueous solutions (pH 8–10) were shown to catalyse C_2H_2 electroreduction to C_2H_4 and C_2H_6 with the $C_2H_4:C_2H_6$ ratio of 4 : 5. In this system, as well as in the others to be discussed below, C_2H_4 is not reduced, and C_2H_6 formation from C_2H_2 thus takes place without the withdrawal of the C_2H_4 derivative from the catalyst coordination sphere.

Similar catalytic activity is displayed by Mo(III)–citrate complexes [74]. A vacancy for C_2H_2 coordination is assumed [73,74] to become available as a result of the breaking of the oxo-bridge bonds between the molybdenum(III) ions in the dimeric complex formed upon the reduction of the initial Mo(V)–cysteine or Mo(V)–citrate complexes. This conclusion is in good agreement with the fact that the $[Na_2MoO_4(edta)]$ complex (edta = ethylenediaminetetraacetate), in which no such breakage of bonds occurs after the molybdenum(VI) reduction to molybdenum(III), is catalytically inactive [73]. However, as a result of the oxo bridges being replaced by more labile sulphide bridges in $[Na_2Mo_2O_3S(edta)]$ or $[Na_2Mo_2O_2S_2(edta)]$, the breakage of the bridges becomes possible again, and catalytic activity appears. This raises the selectivity with respect to C_2H_6, and the $C_2H_4:C_2H_6$ ratio of 0.2–0.3 differs sharply from that characteristic for cysteine and citrate complexes.

When magnesium ions were introduced into a system containing Mo(III)–citrate complexes, the current yield of the reaction products became quantitative, and the selectivity with respect to C_2H_6 increased [74]. Thus it was assumed that the two molybdenum(III) ions, on being brought closer together owing to the elongated bridge formed by the carboxylate bidentate ligand or the magnesium ion, created a possibility for C_2H_2 linear coordination between the molybdenum ions. This coordination is similar to the nitrogen coordination considered above and facilitates a more effective C_2H_2 reduction to C_2H_6 via an intermediate dimolybdenum derivative:



Together with C_2H_4 and C_2H_6, appreciable quantities of methane, propane and propene were observed [75,76] in the products of the amalgam reduction of C_2H_2 in the presence of Mo(III)–citrate and W(III)–citrate complexes. The formation of CH_4 indicated an increase in the lifetime of the dimetallic C_2H_6 derivative M=CH–CH=M, owing to a decrease in the proton donor properties of the medium, as a result of which its further reduction, with the cleavage of the C–C bond, became possible [75]. This cleavage is assumed to be accompanied by the formation of carbenoid intermediates of the $M{=}CH_2$ type, whose secondary reactions with C_2H_2 lead to the appearance of propane and propene in the reaction products [76].

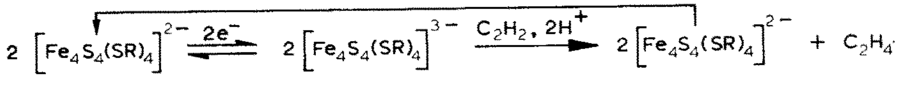
In the above electrocatalytic systems the reaction rate depended exponentially on the cathode potential, and thus the rate-determining step was the electron transfer from the electrode to the catalytically active species containing the coordinated C_2H_2 molecule. In contrast with this, in a system that included Ti(III)–catechol and Mo(III)–catechol complexes the reaction rate no longer depended on the cathode potential, and was higher by about an order of magnitude than in a system without titanium(III) [77]. As in the case of the amalgam reduction of nitrogen [47], $\mathrm{Ti(cat)}_3^{3-}$ (where cat = catechol) is assumed to play the part of a mediator that transfers electrons from the electrode to the molybdenum(III) catalytically active species in the bulk of the solution.

In ref. 78 the Fe–Mo cofactor isolated from nitrogenase was used as the catalyst for C_2H_2 electroreduction. 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 catalysed the same reaction, but only in the presence of adenosine trinucleotide phosphate and methyl viologen as mediator, because direct electron transfer from the electrode to the enzyme active centre was prevented by its protein environment.

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

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

where $R = C_6H_5$ or *n*-MeC_6H_4 [79], was used to create an electrocatalytic cycle in which the reduced form of the cluster was continuously regenerated at a mercury cathode [80]: 3



Scheme 3.

The attitude to the conclusions regarding the role of Fe–S and Fe–Mo–S clusters in electrocatalytic reactions should be cautious, since their reduction can be accompanied by dissociation or decomposition of the cluster into low molecular weight fragments. In particular, according to the data in ref. 81, in $FeCl_2$–CH_3OH (or $FeCl_3$–CH_3OH) and Li_2S–CH_3OH solutions the sodium amalgam reduces C_2H_2 to C_2H_4 and C_2H_6 with an activity close to that of the $[Fe_4S_4(SBu)_4]^{2-}$ cluster which decomposes under the conditions of amalgam reduction.

The modification of the surface of an electrode prepared from polymeric sulphur nitride $(SN)_x$ with molybdenum ions (possibly by means of binding them with the surface sulphur atoms) made it possible to obtain a chemically modified electrode at which C_2H_2 was selectively reduced to C_2H_4 with a quantitative current yield and an activity exceeding that of nitrogenase [82].

Electrocatalytic systems based on molybdenum complexes were also used to reduce other substrates with triple bonds. For instance, in the presence of Mo(III)–citrate complexes at a mercury cathode at a potential of -1.8 V, cyanide ion was reduced to NH_3. Moreover, CH_4 and C_2 and C_3 hydrocarbons were found in small quantities [83]. In CH_3CN reduction in the same system, propane and propene were found, along with the main products C_2H_6 and NH_3, which is indicative of the breaking of the C–C bond in the activated CH_3CN molecule with the intermediate formation of, most probably, an $Mo{=}CH_2$ carbenoid fragment. There is then carbon chain growth as $Mo{=}CH_2$ interacts with the next CH_3CN molecule [84]. No amines were observed to form in these systems.

The above-mentioned Fe–S and Fe–Mo–S clusters in protic media catalyse the reduction of methylisonitrile to CH_4, C_2H_4 and C_2H_6, and of CH_3CN to C_2H_6, C_2H_4 and NH_3 [85]. Under the same conditions the azide ion is reduced to N_2H_4, NH_3 and N_2 [86], and from RN_3 ($R = CH_3$, HOC_2H_4), N_2H_4, NH_3 and RNH_2 are formed [87]. The reduction can be carried out, for example, 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 CH_3CN solution onto the surface of a conducting support. However, the activity of such an electrode drops with time because of the cluster desorption from its surface [87].

(iii) Reduction of carbon and nitrogen oxides

The development of catalysts for low temperature reduction of CO and CO_2 is potentially of great importance, since with the exhaustion of coal, oil and natural gas reserves, carbon oxides may become the source of raw materials for the synthesis of various organic compounds.

The questions regarding the coordination chemistry of the CO_2 molecule and its biological, chemical, photochemical and electrochemical activation are elucidated in recent reviews [88]. Amalgam or electrochemical reduction of CO_2 in the absence of metal complexes, depending on the conditions (electrode material, solvent etc.), can result in different types of products: formates [89], oxalates [89,90] and a number of other organic compounds (tartrate, glycolate etc.) [88].

The CO_2 electroreduction that is not catalysed by metal complexes requires large amounts of energy, since the reduction of CO_2 to the radical anion $CO_2^{\cdot-}$, which is the primary product of CO_2 conversion into useful products, is accomplished at potentials of about -2 V [88]. The situation can change radically when metal complex catalysts are used. Already mentioned above were studies involving CO_2 in the electrocatalytic reaction of organic halide carboxylation [17]. Another reaction catalysed by metal complexes is the reduction of CO_2 to CO. The catalysts used in this reaction are tetraazamacrocyclic complexes of cobalt [91] and nickel [92], $Re(bpy)(CO)_3Cl$ [93], $[Ru(bpy)_2(CO)_2]^{2+}$ [94], $Rh(diphos)_2Cl$ [95] and others. The reaction is carried out in aqueous-organic or aqueous media at atmospheric or elevated CO_2 pressure at various electrodes (mercury, glassy carbon, platinum etc.). The product of CO_2 reduction is a mixture of CO and H_2, and under optimum conditions the current yield of CO reaches 90–100%. In alkaline media, formate is produced as well as CO [94].

The electrolysis is performed at the potentials of the metal complex electroreduction. In all cases these potentials are more negative than the thermodynamic potential for CO_2 reduction to CO [88]. The complexes retain their catalytic activity over a long period of time [92–95]. Metal complexes are assumed [93] to act as redox catalysts in this reaction. Since this reaction is in fact the reverse of the metal-complex-catalysed water gas ($CO + H_2O$) conversion reaction [96], metal complexes in the electrocatalytic conversion of CO_2 into CO play a role not only in the electron transfer from the electrode to the CO_2 molecule but also in CO_2 pre-coordination and activation. The absence of formate in the products is, in the authors' opinion [93], indicative that no hydride derivatives capable of reducing CO_2 to formate are formed in the reduction of metal complexes.

In ref. 97 it was shown that the $Rh(bpy)_2^+$ complex, electrochemically generated from $[Rh(bpy)_2(CF_3SO_3)]^{2+}$ in MeCN at the redox-transition potentials of $Rh(bpy)_2^{0/-}$ ($E^\circ = -1.55$ V), catalytically reduces CO_2 at atmospheric pressure to formate with a current yield of 64%. The formation of the products is described in a stoichiometric scheme with the participation of the background electrolyte cation:

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

In the same study it was shown that under similar conditions the complex

Ru(trpy)(dppe), electroregenerated by the irreversible two-electron reduction of $[Ru(trpy)(dppe)Cl]^+$ (where trpy = 2,6-bis(2-pyridyl)pyridine), catalyses CO_2 reduction in accordance with the following stoichiometric scheme:

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

It is assumed that the catalytic activity of polypyridyl complexes of metals is caused by the possibility of their electroreduction, accompanied by the ejection of $CF_3SO_3^-$ or Cl^- anions with the appearance of a vacant site for CO_2 binding in the coordination sphere. The further reduction of CO_2 in the coordination sphere leads to products the nature of which depends essentially on the basicity of the intermediates of CO_2 reduction. A substantial role in the catalytic activity of these complexes seems to be played by polypyridyl ligands acting as a kind of "electron reservoir" [97].

The $[Fe_4S_4(SR)_4]^{2-}$ cluster (where R = Ph, $PhCH_2$), which has the cubane structure and is a model of ferredoxin, catalysed CO_2 electroreduction on mercury in DMF at $E = -1.7$–2.0 V, forming formate, oxalate and CO as the products [98]. The same products are also formed in the non-catalytic reaction of CO_2 electroreduction but at considerably more negative potentials (-2.4 V). Moreover, the non-catalytic reduction of CO_2 results mainly in oxalate, whereas in the catalytic process the main product is formate (selectivity up to 93%). By varying the electrolyte composition the process can be directed towards the desired product.

The use of transition metal compounds capable of forming complexes with CO_2 can thus provide a specific catalytic mechanism of reduction. More promising is the CO_2 reduction to formaldehyde, methanol and hydrocarbons, with the reaction desirably conducted in protic media. Only the first steps have been taken in this direction. For instance, in ref. 99 it was shown that in CO_2 reduction with zinc amalgam, catalysed by VO^{2+} ions, in acid aqueous solutions (pH 2.5), formic acid as well as formaldehyde, methanol and methane are formed. In the presence of titanium ions, aluminium amalgam selectively reduces CO_2 only to formaldehyde under normal conditions [100]. The reaction proceeds in a narrow pH interval of about 3.5, which allowed the authors [100] to make an assumption about the nature of the catalytically active species, consisting of an associate of two titanium ions.

The molybdenum(III) complex with catechol catalyses the electroreduction of CO_2 at a mercury cathode to C_1–C_3 hydrocarbons [101]. The reduction was conducted in an aqueous buffer solution (pH 7) under the conditions of galvanostatic electrolysis ($i = 7$ mA cm^{-2}). The reaction is accompanied by intensive hydrogen evolution, and the overall yield of hydrocarbons does not exceed 0.2%. It is of interest that no formation of oxygen-containing products of CO_2 reduction (CO, formaldehyde, formic acid and methanol) was observed. The reaction rate increased fivefold upon the introduction into the system of $Ti(cat)_3^{3-}$, which is itself inactive with respect to CO_2. The reduction of CO_2 is assumed to take place inside the molybdenum(III) coordination sphere and follows the mechanism of inner-sphere catalysis without the intermediate products entering into the bulk of the solution. This system is also interesting because, along with inner-sphere catalysis, outer-sphere redox catalysis also occurs, since $Ti(cat)_3^{3-}$ acts as a carrier transferring the electrons from the cathode [47,77].

Formation of C_1–C_3 hydrocarbons was also observed in CO_2 reduction catalysed by $[Fe_4S_4(SR)_4]^{2-}$ [98].

Other classes of transition metal complexes catalysing the electroreduction of CO_2 are metallophthalocyanines and metalloporphyrins. These are discussed in greater detail in ref. 3. The main products of reduction are oxalic and gluconic acids.

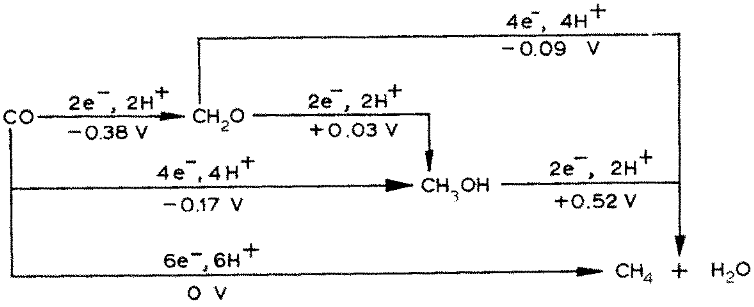
One can also mention the study [102] where $VO(acac)_2$ in MeCN was shown to catalyse CO_2 electroreduction at the potentials of the corresponding vanadium(II) complex generation; the reduction products, however, were not identified.

Thus the possibility of the formation of CO_2 complexes with transition metal compounds and the possibility of inner-sphere electron transfer onto the coordinated CO_2 molecule at considerably more positive potentials than in pure electroreduction are indicative of the promising use of metal complex catalysis for various CO_2 conversion reactions.

The involvement of CO in catalytic reactions for the synthesis of organic compounds has for a long time been applied not only in fundamental research but also in industry. Suffice it to note the Fischer–Tropsch processes of obtaining synthine, the methanol carbonylation to produce acetic acid, water gas conversion etc. [2]. The study of the electrochemical conversion of CO began fairly recently. The electroreduction of CO takes place at extremely negative potentials, as the thermodynamics of this process seem to be most often determined by the potential of CO reduction to the $CO^{\bar{\cdot}}$ radical anion. Thus CO can be chemically reduced only with an Na–K alloy in THF [103]. Here the final products formed after hydrolysis of the reaction mixture are the anions of glycolic and oxalic acids, as well as $C_3O_3^{2-}$. The CO electroreduction at a pressure of several hundred atmospheres on a steel electrode under the conditions of galvanostatic electrolysis produces squaric acid ($C_4O_4H_2$) [104]. Finally, in liquid ammonia (−50 °C) in the presence of 0.1 M KI, CO is reduced at various cathodes at potentials close to the potentials of solvated electron (e_s^-) generation [105]. However, an attempt at CO preparative electroreduction under these conditions gave no positive result. It is only the reduction of CO by electrogenerated e_s^- that results in the production of $C_2O_2^{2-}$ dimeric anions which precipitate as the $K_2C_2O_2$ salt.

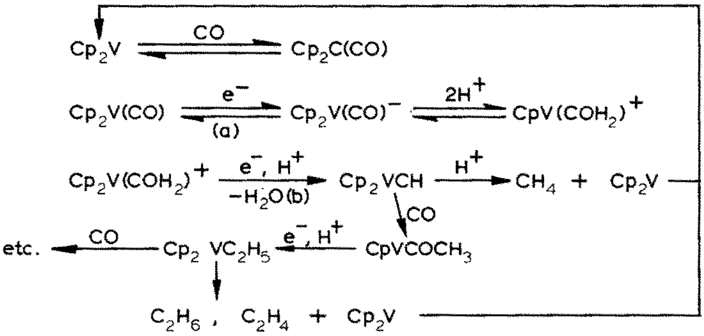
A change-over to multielectron reactions must improve substantially the CO reduction energetics. The thermodynamics of CO reduction to the simplest organic compounds confirm this.

Despite the favourable thermodynamics, direct amalgam or electrochemical reduction of CO at a mercury cathode is impossible, most probably because of kinetic limitations. The picture changes radically in the case of CO coordination with transition metal complexes, i.e. under the conditions of coordination electrocatalysis, when it is the catalyst–substrate complex with an activated CO molecule which is being reduced.



Scheme 4.

The fruitfulness of this approach was first demonstrated in the amalgam reduction of CO to C_1–C_4 hydrocarbons, catalysed by vanadocene [103–110]. It was shown [106,107] that Cp_2V at room temperature and atmospheric pressure of CO in aprotic solvents (DMF, THF etc.), containing diethylbarbituric acid or phenol as proton donors, effectively catalyses CO reduction with sodium amalgam. Methane (85–95%) is formed as the principal product, with the simultaneous formation mainly of saturated C_2–C_4 hydrocarbons. Under optimum conditions, more than 100 molecules of hydrocarbons are formed per one molecule of the catalyst, and periodic addition of the expended reagents (amalgam, CO and the proton donor) to the system makes it possible to accomplish a continuous process for the synthesis of hydrocarbons from CO [106]. This reaction, constituting as it were an electrochemical analogue of the Fischer–Tropsch synthesis, proceeds with the participation of adsorbed catalyst and is characterized by the endoergonic transfer of the first electron onto the molecule of the coordinated substrate since $E^{\circ}_{Cp_2V(CO)^{0/-}} = -2.3$ V, while the amalgam potential is about −2.1 V [109]. This is the first experimentally proved case known to us of the endoergonic transfer of an electron [6] in metal complex electrocatalysis. Vanadocene also catalyses hydrogen evolution in this system, as a result of which the current yield of hydrocarbons does not exceed 10% [108]. Both the reactions (CO reduction and H_2 evolution) take place in the adsorption layer without the intermediate reduction products entering into the bulk of the solution, and their kinetics are described not with the volume concentration but with the surface concentration of the catalyst taken into account. The CO reduction occurs at potentials that are insufficient for the intermediate formation of the hydride Cp_2VH^-, which thus excludes a possible hydride mechanism for CO reduction and explains the absence of CH_2O and CH_3OH in the reaction products [107,108]. Finally, the formation of C_2–C_4 hydrocarbons, as well as the hydrocarbon chain propagation in the Fischer–Tropsch synthesis, are accomplished by means of CO insertion into the metal–alkyl bond in the vanadocene alkyl complexes formed as intermediates [109]. This once again indicates that the general regularities of metal complex catalysis are preserved in electrocatalysis. The catalytic cycle of vanadocene-catalysed CO electroreduction can be represented by the following scheme [109,110]:



Scheme 5.

where stage (a) is endoergonic and occurs owing to a fast and irreversible stage (b) with the breaking of the C–O bond.

The efficiency of metal complex electrocatalytic systems depends substantially on the catalyst stability. Thus, along with vanadocene, other electrogenerated metallocenes of groups VB and VIB also catalyse CO electroreduction in aprotic solvents that contain proton donors, but the catalytic activity of the systems based on these drops to zero fairly fast [111]. This drop is caused by the metastability of Cp_2M complexes (M = Nb, Mo, W) responsible for the coordination with CO. For fundamental research the advantage of electrocatalytic reactions is that electrochemical methods can be used to study them. For the CO electroreduction catalysed by metallocene dichlorides, the authors [111,112], using electrochemical methods, succeeded not only in identifying the primary products of the catalyst interaction with CO and drawing conclusions about the nature of the catalytically active species, but also in elucidating the cause of the differences in the catalytic activity of Cp_2MCl complexes (M = Ti, V, Nb, Mo, W). This is associated with the different stabilities of the metallocenes and their cations which are responsible for coordination with CO. They also succeeded in characterizing the kinetic and thermodynamic regions of their stability. The region of thermodynamic stability of catalysts is an important factor to be taken into account in developing metal complex electrochemical systems. Without taking this factor into account one can over-reduce, or vice versa, oxidize the catalyst, as a result of which the electronic configuration of the metal in it will change and prove to be unfavourable for substrate coordination, and the catalyst will lose its activity. Worthy of notice in this connection are studies [113–115] where for sandwich and bent-sandwich metal complexes, catalytically active in numerous reactions [67,116], predictions were made of the regions of thermodynamic stability of neutral and ionic metal complexes from the tabular values of the ionization potentials of the corresponding metals.

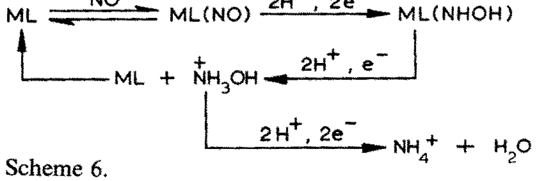
The CO electroreduction to C_1–C_3 hydrocarbons can also be accomplished in aqueous solutions ($6 < pH < 13$) using the Mo(III)–catechol complex adsorbed on a mercury cathode as the catalyst [117]. As in non-aqueous systems, the main product is methane (80–90%), and the overall current yield of hydrocarbons amounts to fractions of one per cent, since the main quantity of electricity is consumed in the parallel H_2 evolution reaction, catalysed by the same molybdenum(III) complexes. The efficiency of this system rises considerably when $Ti(cat)_3^{3-}$ is introduced into it, which is manifested by an increase in the reaction rate and in the current yield of hydrocarbons to 15% [118]. On the basis of the results of a kinetic and electrochemical study of this system it was concluded that the species catalytic with respect to CO is the Mo(III)–carbonyl complex, and the redox couple $Ti(cat)_3^{2-/3-}$ acts as the redox catalyst. Thus, with a redox catalyst introduced into the system, a possibility also appears for electron transfer onto molybdenum(III) complexes which activate the CO molecules but have no direct contact with the electrode, and as a result the overall reaction rate increases. This is an excellent example of a combination of coordination (CO activation and inner-sphere reduction on the molybdenum(III) complex) and redox catalysis (electron transfer from the $Ti(cat)_3^{3-}$ complex to the Mo(III)–carbonyl complex), resulting in an increase in the catalytic efficiency of the system.

Apart from the electrocatalytic reduction of CO to hydrocarbons already considered, CO electroreduction to oxygen-containing products, catalysed by metal complexes, is also possible. At room temperature and atmospheric pressure, CO in aqueous solutions (pH 3.5) is selectively reduced to methanol at a platinum electrode modified by the complex $[Fe^{II}(CN)_6Fe^{II}K_2]$ (**III**) at $E = -0.9$ V [119–121]. Methanol is also formed on a non-polarized cathode, which is accompanied by the oxidation of the complex **III** into

$[Fe^{II}(CN)_6Fe^{III}K]$ (**IV**). The CO molecule is assumed to be activated because of its inclusion into the $[Fe(CN)_6]^{4-}$ anion coordination sphere, with the displacement of CN^- and the formation of $[Fe(CN)_5CO]^{3-}$, and the further reduction of CO to CH_3OH follows the redox catalysis mechanism (catalyst–(redox couple **III**/**IV**)) [119,120].

Relatively few data are available on CO electro-oxidation catalysed by metal complexes. One can only mention here the study in ref. 122 where $[Rh(CO)_2X_2]^-$ complexes in aqueous solutions of HX (X = Cl, Br, I) are shown to catalyse CO oxidation to CO_2 on glassy carbon at potentials of about 0.4 V. This reaction is regarded as a promising reaction for use in fuel cells.

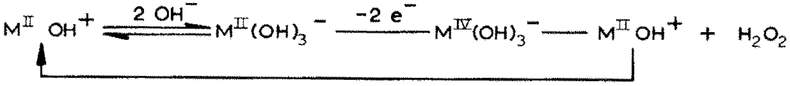
The interest in the problem of electrocatalytic reduction of NO is associated with the attempts to utilize, under mild conditions, the nitrogen oxides contained in the waste gases of numerous industrial chemical processes. In contrast with the conventional methods of NO heterogeneous reduction with the help of H_2, CO or NH_3 (see for example ref. 123), the electrochemical utilization of NO does not require high pressures and temperatures. Successful attempts have been made at both the direct NO electroreduction and that in the presence of metal complexes to produce N_2O, N_2, NH_2OH, N_2H_4 and NH_3 [123,124]. The study in ref. 125 shows that in weakly acid aqueous solutions in the presence of the edta complexes of transition metals (Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} etc.), the electroreduction of NO at a semiconducting GaAs electrode is accompanied by selective NH_3 formation (22–31% conversion) at room temperature and atmospheric pressure. Similar results were obtained at a platinum electrode ($E = -1.8$ V) using FeL_3^{2+} complexes (L = phen, bpy) as the catalysts; conversion of NO into NH_3 was 77–84% [126]. Finally, at a glassy-carbon cathode modified with cobalt phthalocyanine the selectivity of NO conversion into NH_3 reaches 92% (current yield, 63%), whereas at a platinum electrode modified with the Fe^{2+}–poly(4-vinyl pyridine) redox catalyst the selectivity does not exceed 2% [127]. This testifies in favour of the NO reduction more probably following the coordination and not the redox mechanism. It may be assumed that NO coordination with the metal is accompanied by an electron density redistribution on the NO molecule, as a result of which it is activated and reduced. Then the scheme for the NO reduction to NH_3, catalysed by metal complexes (ML) can, for example, be represented as follows [126,128]:



Scheme 6.

(iv) Oxidation of water and organic compounds

The oxidation of water to oxygen is a complex multielectron process. It imposes certain requirements on the metal complex catalysts for these reactions, which are very similar to the requirements imposed on the nitrogen reduction catalysts: it is necessary for the metal complex to be able to "switch" the thermodynamically unfavourable one-electron mechanism over to the more favourable multielectron process [129–131]. It is only in this case that the thermodynamics of the overall oxygen formation process become sufficiently favourable. In ref. 129, by analogy with natural photosynthesis, it is assumed that the metal complex must constitute a binuclear or tetranuclear cluster, every atom of which is capable of accepting respectively two or one electrons, and what is more, reversibly, because only then can the catalyst be efficient. The use of mononuclear complexes as catalysts is also possible. In this case, however, water oxidation will proceed via the intermediate formation of a peroxide derivative, and only if the metal atom in the complex is able to change its valence by two units. The use of such approaches in refs. 132 and 133 showed simple iron(II) and cobalt(II) hydroxo complexes to be efficient catalysts for the electro-oxidation of water. Efficient functioning of such catalysts is determined by the ability of the metals in the catalysts to change their valence by two units with the formation of highly reactive M(IV) complexes oxidizing water to a peroxide, which under these conditions is rapidly oxidized or catalytically decomposed on the electrode with the formation of oxygen. The mechanism of the electrocatalytic oxidation of water with the participation of iron or cobalt hydroxo complexes (MOH^+) is illustrated in the following scheme [132,133]:



$$M^{II}OH^{+} \xrightleftharpoons{2\,OH^{-}} M^{II}(OH)_3^{-} \xrightarrow{-2\,e^{-}} M^{IV}(OH)_3^{-} \longrightarrow M^{II}OH^{+} + H_2O_2 \tag{1}$$

Scheme 7.

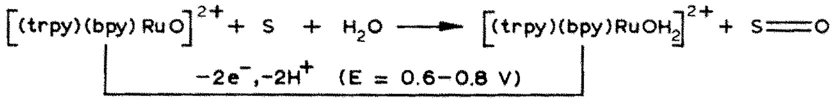
The catalytic electrode process seems to be of a mixed volume–surface nature, though the appearance of a catalytic oxidation wave on voltammograms already at Fe^{2+} and Co^{2+} concentrations of 10^{-8}–10^{-6} mol l^{-1} indicates a significant contribution of the volume process to this reaction [132].

The development of water-oxidation catalysts is also of great importance from the viewpoint of solving the problem of the photocatalytic oxidation of water. In particular, iron and cobalt hydroxo complexes were used to devise some of the first photocatalytic systems of water oxidation under the action of visible light to give high quantum yields [134,135]. On the basis of a detailed kinetic study of the mechanism underlying the catalytic action of these hydroxo complexes in the oxidation of water by one-electron oxidants, it was concluded in refs. 136–139 that the mechanism of the process is more complex than that represented by the overall equation (eqn. (1)).

In subsequent studies, the authors tried to use the complexes of the same transition metals, but with other ligands, as homogeneous catalysts for electrochemical and chemical water oxidation. The high activity of even trace quantities of hydroxo complexes led, in our opinion, to a wrong interpretation of the data obtained. Thus in ref. 140 a conclusion was drawn that the hypothetical complex $[Fe(bpy)_2(bpyH)OH]^+$ is a catalyst for water electro-oxidation. The authors, however, did not take into account the fact that in alkaline media the initial $Fe(bpy)_3^{2+}$ complex is hydrolysed with the formation of $FeOH^+$ in quantities sufficient for the catalytic effect to appear [132]. A similar mistake was also most probably made by the authors [141,142] when studying the chemical oxidation of water by one-electron oxidants. The solutions of iron and cobalt complexes with various ligands, used by them as catalysts, practically always either contain trace quantities of the corresponding hydroxo complexes or are hydrolysed with their formation. According to the data in refs. 143 and 144, these quantities are quite sufficient for the catalytic effect observed in refs. 141 and 142.

The binuclear complex $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$ (**V**) is reported [145,146] to oxidize water to oxygen in an electrochemical four-electron oxidation to $[(bpy)_2(O)Ru^{V}ORu^{V}(O)(bpy)_2]^{4+}$ in an acid medium. The authors note, however, that the initial complex undergoes destruction in the course of the catalytic reaction. It is quite possible that in the course of destruction, $RuO_2 \cdot xH_2O$ is formed, which is known [147] to catalyse effectively the chemical and electrochemical oxidation of water to oxygen in an acid medium. Moreover, the complex **V** catalyses the chemical or electrochemical oxidation of Cl^- to Cl_2 [148,149]. For this reason, among others, the authors [145] initially drew the wrong conclusion about the catalytic activity of the dimer **V** in the water electro-oxidation, since trace quantities of Cl^- were present in the electrolyte solution.

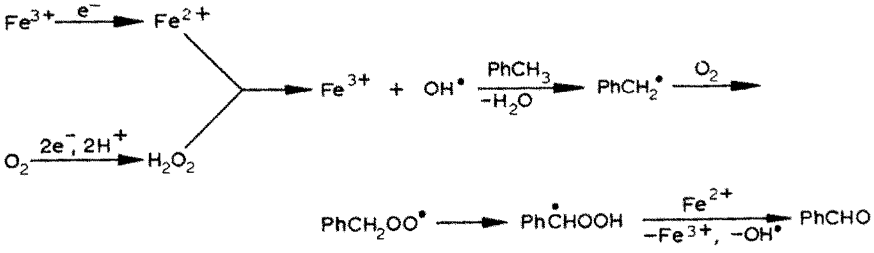
Thus, despite some progress elucidating the catalytic activity of iron(II) and cobalt(II) hydroxo complexes [132,133], the problem of developing metal complex catalysts for water oxidation is still far from solved. Organic compounds can be oxidized with the participation of a number of transition metal ions of higher oxidation state (Co^{3+}, Ce^{4+}, MnO_4^-, Mn^{3+}, $Cr_2O_7^{2-}$, Tl^{3+}). Some of these reactions can be used to create an electrocatalytic cycle where the transition metal ion is regenerated to its 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 frequently this operation is performed in a separate electrolyser, and the substrate is then oxidized in a separate reactor. An analysis of reactions which involve electrochemically generated oxidants is beyond the scope of this review. The necessary information can be obtained from a monograph [4] and reviews [150,151]. We shall therefore consider only two examples of the use of metal complexes in oxidation reactions. The first example refers to the use of Ru(IV)–polypyridyl complexes as redox catalysts for the oxidation of organic compounds (S) [152] according to the following scheme:



Scheme 8.

The oxidation is carried out in a diaphragm cell at a glassy-carbon anode in a phosphate (pH 7) or a borate (pH 9) buffer solution at metal complex concentrations of about 10^{-3} mol l^{-1}. Under these conditions it is possible to oxidize propan-2-ol to acetone, toluene to benzoic acid, *p*-xylene to terephthalic acid, and cyclohexene via the intermediate formation of cyclohexen-2-one to *p*-benzoquinone. The oxidation can be carried out not only with the use of a dissolved metal complex but also with its pre-immobilization on the anode surface [153].

The second example concerns the cathodic oxygen activation reactions with the participation of metal complexes or transition metal ions. Such activation can be accomplished by reducing oxygen to H_2O_2 and generating from it the $OH^{\cdot}$ radical by means of H_2O_2 reaction with Fe^{2+} ions (Fenton's reagent). On the basis of this principle the electrocatalytic systems for the oxidation of polymethylated benzenes to the corresponding aldehydes [154], as well as of C_5–C_{30} aliphatic hydrocarbons and 3-methylpentane to ketones were constructed [155]. The electrolysis is conducted in oxygen-saturated aqueous solutions of hydrochloric acid at a mercury cathode. The mechanism of the catalytic cycle is assumed to be as follows [154]:



Scheme 9.

Electrochemical oxygen activation in hydrocarbon oxidation reactions was also successfully accomplished by means of electron transfer to the iron-porphyrin complex immobilized 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 oxidized under the conditions of potentiostatic electrolysis at $E = -1.5$ V to the corresponding hexanols in MeCN containing 10% of the hydrocarbon and 5×10^{-2} mol l^{-1} of acetic anhydride. The current yield of the alcohol was 7%. In the course of electrolysis the system lost its activity, and after 2 h the reaction stopped completely because of the iron porphyrinate having been washed off from the cathode. It is assumed that the oxidation of hydrocarbons (RH) at this electrode is described by the following sequence of reactions (P = porphyrin):

$$\begin{tikzcd}
\mathrm{PFe^{III}} \arrow[r, "e^-"] & \mathrm{PFe^{II}} \arrow[r, "e^-"] \arrow[d, "O_2"] & \mathrm{PFe^{I}} \arrow[d, "O_2"'] & & \\
& \mathrm{PFe^{III}O_2^-} \arrow[r] & \mathrm{PFe^{III}O_2^{2-}} \arrow[r, "Ac_2O", "-AcO^-"'] & \mathrm{PFe^{III}OOAc} \arrow[r, "-AcO^-"] & {}
\end{tikzcd}$$

$$[\mathrm{PFe^{IV}{=}O}]^+ \xrightarrow{RH} \mathrm{PFe^{III}} + \mathrm{ROH}$$

where the $[\mathrm{PFe^{IV}{=}O}]^+$ oxo complex acts as the hydrocarbon-oxidizing agent. On the whole the catalytic cycle can be regarded as an electrochemical model of cytochrome P-450.

(v) Dimerization and metathesis of olefins, electrodimerization of carbonyl compounds and other reactions

In recent years, electrochemical methods have also found application in the synthesis of selective catalysts for 1,3-diolefin cyclodimerization [157–159] and for the metathesis [160,161] and dimerization [162] of olefins, starting from complexes of iron, tungsten and nickel respectively, with the electrolysis mainly used in these cases to generate the initiators of the above reactions.

As already noted [9–11,163], Ni(0)–triarylphosphine and Ni(0)–trialkylphosphine complexes react with RX to form electroactive organometallic compounds, from which, under the conditions of electrolysis, the R–R dimerization products can be obtained under sufficiently mild conditions. Moreover, by appropriate selection of the conditions (solvent, phosphine-to-nickel ratio etc.) it is possible to include olefins and CO_2 into the reactions that lead to the formation of compounds with new C–C bonds [164–167]. In the absence of current, these reactions are not catalytic and require continuous electrochemical generation and regeneration of nickel(0) promoters. These then enter into oxidative addition reactions with the substrates in the catalytic cycle, forming σ Ni^{2+} organic derivatives which undergo subsequent chemical and electrochemical conversion into the desired products (see, for example, the dehalogenation reactions). In contrast with the electrically generated promoters, some other nickel-containing complexes obtained by electroreduction are true catalysts and require no additional electricity expenditure for the regeneration of the active species. This is the case in the cyclo-oligomerization of dienes, in the course of which it is sufficient for the active nickel and iron complexes to be electrochemically generated only initially [157–159,168]. The catalytic activity of these electrochemical systems is not inferior to that of similar chemical systems obtained under the action of organoaluminium compounds which function as a co-catalysts. The co-catalytic action of organoaluminium compounds is caused both by their strong reductive properties and by their ability to accept halide ions [169]. The Ni^+ phosphine halide complexes can serve as an example of such an electrogenerated catalyst. They catalyse ethylene and propylene dimerization to products with an internal double bond [162]. The catalyst is generated by Ni^{2+} electroreduction (gold or platinum cathodes) in the presence of PPh_3 and Cl^- in propylene carbonate medium in a diaphragmless cell with sacrificial anodes (zinc, cadmium, aluminium).

Activated $H_2C{=}CHX$ olefins (acrolein, methyl vinyl ketone, styrene and others) are polymerized in aprotic media at the potentials of $Ni(phen)_3^{2+}$ electroreduction to the nickel(0) complex. The electrogenerated $[Ni(-1)(phen)(olefin)]$ complex is assumed [170] to be the catalyst.

In the presence of chromium, manganese and tungsten complexes the electroreduction of carbonyl compounds is accompanied by the formation not only of alcohols or pinacols [171], products of direct electrode reactions which are classical for these substrates, but also of olefins [172] that are not formed in the absence of metal complexes. Thus reduction of carbonyl compounds (benzaldehyde, benzophenone, acetophenone, acetone, propionic aldehyde) in THF at a platinum electrode in a diaphragmless cell with sacrificial anodes (aluminium, zinc, iron) is accompanied by selective reductive dimerization of aldehydes and ketones with the formation of olefins (stilbene, tetraphenylethylene, 1,2-dimethoxystilbene, tetramethylethylene, 3-hexene respectively). The yield of olefins, depending on the nature of $R_2C{=}O$, amounts to 6–99%. It is assumed [172] that $R_2C{=}O$ dimerization is caused by the electrogenerated W^{2+} complex, and the reaction may proceed via the intermediate formation of the 18-electron complexes $[WCl_6(R_2CO)_2]$. In CH_2Cl_2 medium the $[W]{=}CH_2$ carbene complex, formed under the conditions of WCl_6 electroreduction, reacts with benzaldehyde to form styrene [172].

Among other reactions catalysed by metal complexes is the nitromethylation of benzene by nitromethane to produce benzyl nitrate. The reaction is conducted in AcOH and is catalysed by the Mn^{3+} complex electrogenerated from Mn^{2+} [173].

The products of the electroreduction of NiL_3^{2+} complexes (L = phen, bpy) in DMF catalyse acrylonitrile polymerization [174].

In recent years it has become important to study the electrochemical synthesis of homogeneous and heterogeneous catalysts from metal complexes for use in the conversion of various organic compounds. In addition to the olefin cyclodimerization and metathesis reactions already examined, we shall note a number of other studies. For instance, the homogeneous catalyst "$[Rh(CO)(Ph_3P)_2]^-$", generated by two-electron reduction of the complex $[RhCl(CO)(Ph_3P)_2]$ (platinum cathode; propylene carbonate), catalyses the hydroformylation reaction of 1-hexene to 2-methyl-2-hexanol under mild conditions ($P_{H_2} = P_{CO} = 1$ atm, 25 °C) [175]. Heterogeneous catalysts with a low metal content (about 1×10^{-4} g Ni cm^{-2}), obtained by electrolytic deposition of nickel on different supports, hydrogenate nitriles fairly efficiently in DMF, but are poorly active with respect to carbonyl compounds [176]. Systems based on metal complexes (rhodium, ruthenium, iron, cobalt etc.) in combination with NAD^+ (nicotinamide adenine dinucleotide) have been developed for the electroreduction of carbonyl compounds to the corresponding alcohols with a high current yield [177]. Finally, by means of aluminium anodic dissolution in an alkyl halide medium, catalysts are obtained for the Friedel–Crafts alkylation of benzene and other aromatic hydrocarbons [178].

D. CONCLUSIONS

The number of studies of the electrocatalytic reduction of CO_2 to CO sharply increased. The following complexes are used as catalysts in an MeCN medium in the presence of various proton donors: $\{Pd[PhP(CH_2CH_2PPh_2)_2]R_3P\}^{2+}$ where R = MeO, Et, Ph, CH_2OH [179], $Ni(dipy)_3^{2+}$, $Ni(dppe)_2^{2+}$ [180], $Re(CO)_3LCl$ where L = dipy and its substituted derivatives [181–184], $Ni(teta)^+$ and Co(salen) [185]. Much attention is given in these studies to the electroanalytical study of the mechanism of the catalytic action of metal complexes. In particular, in ref. 179, CO_2 insertion into the Pd–H bond of the hydride complex, formed as an intermediate in the course of reduction, is shown to be the key stage in the electrocatalytic cycle. The catalytic efficiency and the stability of complexes, substantially increase when the catalyst is fixed on the electrode by the methods of electropolymerization, incorporation into the polymeric matrix etc. [181,183,184]. The electrodes modified with an insoluble $K_2Fe[Fe(CN)_6]$ film catalyse CO_2 and CO reduction to methanol in aqueous media in the presence of water-soluble iron, nickel, cobalt and chromium complexes [186,187]. In MeCN in the presence of $Me_2H_2N^+$ or PhOH as the proton donors the $[Ru(dipy)_2(CO)_2]^{2+}$ complex selectively catalyses CO_2 reduction to $HCOO^-$ [188]. Individual examples of the catalysis of CO_2 reduction reactions, as well as of RX dehalogenation by nickel phosphine, polypyridyl and macrocyclic complexes, can be found in ref. 189.

It has been shown that in principle it is possible to reduce nitrogen by protonation of the $[W(N_2)_2(dppe)_2]$ complex with *p*-toluenesulphonic acid in THF media and subsequent electroreduction under an N_2 atmosphere of the $[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)]^+$ hydrazide cation formed, with the production of NH_3 and the regeneration of the initial dinitrogen complex [190,191]. The products of Cp_2TiCl_2 reduction in THF and MeOH catalyse nitrogen electroreduction to NH_3 [192]. The current yield of NH_3 does not exceed 1.5%, and the results have not been confirmed by blank tests (argon) and tests with $^{15}N_2$.

In aqueous media, cobalt and nickel macrocyclic complexes catalyse NO_3^- electroreduction to hydroxylamine [193], and water-soluble iron porphyrinates catalyse NO_2^- reduction to N_2O, NH_3 and NH_2OH [194,195]; the nitrosyl complex [PFe(NO)] is assumed to be an intermediate product of the latter reaction [195].

A review [196] is devoted to the electro-oxidation reactions of organic compounds, H_2O, Cl^-, as well as to those of NO_2^- reduction, catalysed by ruthenium and osmium polypyridyl complexes. In other reviews [197–199] the uses of metal complexes as redox mediators are examined.

Thus the use of metal complexes in the catalysis of electrode processes makes it possible to reduce energy consumption and to ensure the occurrence of electrochemical reactions of substrates which are electrochemically inactive or are reduced (oxidized) at classical 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 CO_2. The successful development of catalysts for the electrochemical reduction of nitrogen and CO, which makes it possible to reduce these substrates, enables us to consider fundamentally new possibilities in the electrosynthesis of N_2H_4 from nitrogen and organic compounds from CO (i.e. a raw material which is non-traditional for electrosynthesis) at low pressures and temperatures. The use of metal complexes for the catalysis of electrode processes in photoelectrochemical solar energy converters (catalysts for the oxidation of water) and fuel cells (catalysts for the reduction of CO and CO_2 and also for the oxidation of alkanes and CO) is also promising, although it must be admitted 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 owing to a skilful combination of the principles of electrochemistry and of homogeneous and heterogeneous catalysis and the concepts of modern inorganic and organometallic chemistry. It is hoped that the development of this undoubtedly promising field will result in numerous new catalytic reactions and, possibly, facilitate the creation of new industrial processes.

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