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Review

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Molecular Catalysis of Electrochemical Reactions. Mechanistic Aspects

Jean-Michel Savéant*

Laboratoire d'Electrochimie Moléculaire, Unité Mixte de Recherche Universite—CNRS 7591, Université de Paris 7—Denis Diderot, 2 place Jussieu, 75251 Paris Cedex 05, France

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1. Introduction

1.1. "Electrocatalysis" and Molecular Catalysis

Electrochemical reactions often require an important overpotential[1] to proceed at an appreciable rate. This is particularly true when the reaction does not merely consist of an outersphere electron transfer between the electrode and a reactant but gives rise to bond breaking and bond formation, involving more than one reactant and one product, which may trigger the uptake or release of additional electrons, as sketched in Scheme 1.

This is a typical situation where catalysis of the electrochemical reaction is sought in order to increase the reaction rate and hence the current at a potential as close as possible to the equilibrium potential. Several strategies can be envisaged to achieve this goal. The term "electrocatalysis" is traditionally used for reactions in which the electrode material—often, but not always, a metal—is chemically involved in the catalytic process.[2] Although the chemical properties of the electrode material play an important role in governing the catalytic efficiency, geometric and crystallographic features, nature and number of defects, may also be of paramount significance.[3] The differences between the bulk properties of the metal and its surface properties are particularly important in this respect. It is therefore difficult, or even irrelevant, to analyze results and devise new catalytic systems on the basis of molecular concepts.

Another approach to catalyzing electrochemical reactions is to use molecules as catalysts. "Molecular catalysis" thus defined may involve catalyst molecules either homogeneously dispersed in the solution bathing the electrode or

Scheme 1

$$a\,A + b\,B + \ldots \pm n\,e^- \rightleftharpoons c\,C + d\,D + \ldots$$

For example:

$$O_2 + 4\,e^- + 4\,H^+ \rightleftharpoons 4\,H_2O$$

$$H_2 - 2\,e^- \rightleftharpoons 2\,H^+$$

$$CHCl{=}CCl_2 + 2\,e^- + H^+ \rightleftharpoons CHCl{=}CHCl + Cl^-$$

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* E-mail: saveant@paris7.jussieu.fr.

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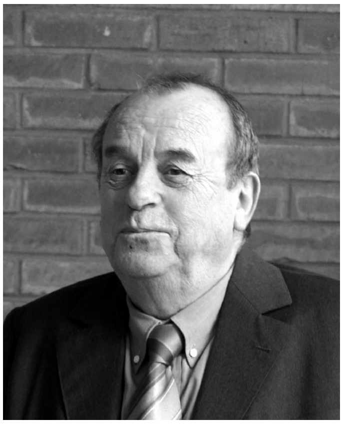


Jean-Michel Savéant received his education in the Ecole Normale Supérieure in Paris, where he became the Vice-Director of the Chemistry Department before moving to the University Denis Diderot (Paris 7) as a Professor in 1971. He is, since 1985, Directeur de Recherche au Centre National de la Recherche Scientifique in the same university. In 1988−1989 he was a distinguished Fairchild Scholar at the California Institute of Technology. His current research interests involve all aspects of molecular and biomolecular electrochemistry as well as mechanisms and reactivity in electron transfer chemistry and biochemistry. Among many distinctions, Jean-Michel Savéant received the Faraday Medal of the Royal Chemical Society, the Olin Palladium Medal of the Electrochemical Society, la Medaglia Luigi Galvani della Società Chimica Italiana and the Manuel Baizer Award of the Electrochemical Society. Jean-Michel Savéant is a member of the French Academy of Sciences and foreign associate of the National Academy of Sciences of the United States of America.

immobilized in a monolayer or multilayered coating deposited on the electrode surface as sketched in Figure 1.

In line with the general theme of this special issue, this review is mostly concerned with molecular catalysis. Nevertheless, discussion of examples of electrocatalysis will not be systematically excluded. Analysis of the similarities and differences between electrocatalysis and molecular catalysis of the same global reaction may indeed benefit from the understanding of the mechanism in each case.

1.2. Redox and Chemical Catalysis. Freely-Diffusing and Immobilized Catalysts. Monolayers and Multilayers

Homogeneous catalysis is concerned with systems in which the catalyst diffuses freely in the solution that contains the substrate.

Testing molecular catalysts implies that the electrode material does not participate in the electrochemical reaction. In other words, the electrode plays the role of a heterogeneous outersphere electron donor (or acceptor). The direct reduction (or oxidation) of the substrate requires a sizable overpotential to give rise to a significant current. The catalyst is usually one member of a reversible couple, P/Q, the standard potential of which is located in between the standard potential of the global electrochemical reaction and the potential where the direct electrochemical reaction occurs. The closer the two standard potentials and the larger the current, the better the catalyst. As exemplified later, catalytic currents may be observed even when the homogeneous electron transfer between the active form of the catalyst is an outersphere reaction. As discussed in the next section, the very existence of “redox catalysis” derives from the fact that, instead of being confined within a two-dimensional space, the electrons to be transferred are then dispersed in a three-dimensional space. “Chemical catalysis” involves more intimate interactions between the active form of the catalyst and the substrate, thus opening a route to more efficient and more specific catalytic processes.

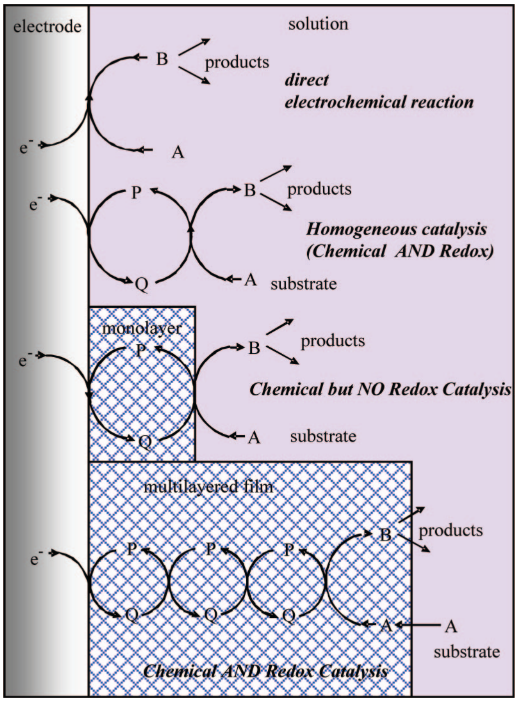


Figure 1. Schematic representation of the various types of molecular catalysis of electrochemical reactions.

In many, but not all, practical applications immobilization of the catalyst molecules onto the electrode surface, as sketched in Figure 1, is advantageous. Catalysis is expected to be more efficient at multilayered coatings than at monolayer coatings, provided transport of electrons, substrate and product through the film does not become rate-limiting. It follows from the very nature of redox catalysis that it is possible in multilayered films but not at monolayer coatings, since redox catalysis implies that the electrons to be transferred be dispersed in a three-dimensional space.

1.3. Synopsis and Connections with Other Contributions in This Issue

Section 2 discusses the techniques that may be used to evaluate a catalyst in terms of efficiency and selectivity.

Section 3 is devoted to the description of a particularly clear example illustrating the distinction between redox and chemical catalysis both in terms of efficiency and specificity. In the fourth section, we review the application of redox catalysis to the kinetic characterization of electron transfer mechanisms involving fast decaying intermediates. Sections 5–7 are dedicated to selected examples where chemical catalysis is particularly important. The examples have been selected in relation with the activation of small molecules relevant to the present challenges of renewable energy and greenhouse effects: reduction of oxygen (section 5), oxygen evolution from the oxidation of water (section 6), reduction of carbon dioxide (section 7). The links that may exist with enzymes that catalyze the same reactions will be emphasized. These enzymes have served as sources of inspiration for the catalyst design or, conversely, the chemical catalyst may be used as a simplified model of the enzyme aiming at a better understanding of enzymatic mechanisms. In spite of its paramount importance, we let aside catalysis of hydrogen evolution and uptake because it is treated in detail in a preceding *Chemical Reviews* thematic issue "Hydrogen".

Numerous other examples, dealing with the organometallic catalysis of important organic reactions, can be found in the contribution of Anny Jutand, to this issue "Contribution of Electrochemistry to Organometallic Catalysis". Reversing the concept of chemical catalysis of electrochemical reactions leads to the notion of using electrons (or holes) from an electrode to catalyze a chemical reaction. This important topic is treated in the contribution of Abdelaziz Houmam, "Electron Transfer Initiated Reactions: Bond Formation and Bond Dissociation". Homogeneous and supported catalysis of electrochemical reactions by enzymes are massively present in the contribution of Christophe Léger "Direct Electrochemistry of Redox Enzymes as a Tool for Mechanistic Studies".

2. Electrochemical Techniques for Catalyst Evaluation

2.1. Preparative Scale Electrolysis and Non-destructive Techniques

Non-destructive techniques, such as cyclic voltammetry operated with a microelectrode, are particularly useful for a first evaluation of the catalyst: determination of the potential at which the catalytic process can be run and of the catalytic efficiency as measured by the current density flowing through the electrode at this potential for a given concentration or partial pressure of the substrate. They may then be used by means of a more detailed kinetic analysis to unravel the mechanism of the catalytic reaction and suggest improvements. Gauging of the selectivity of the catalytic reaction requires moving to preparative-scale electrolysis and determining the faradaic yields of each of the reaction products. Such sustained electrolyses are also necessary to estimate the stability of the catalyst by observing the variation of the preparative-scale current with time. Following the cyclic voltammetric response simultaneously is an additional way of observing the evolution of the catalyst in the course of electrolysis.

Preparative-scale evaluation is thus required to establish the actual performances and viability of catalytic systems beyond the rapid test that cyclic voltammetric allows.

2.2. Cyclic Voltammetry of Free-Diffusing Catalyst Systems

Cyclic voltammetry has been and still is the most popular non-destructive technique applied to homogeneous catalysis systems, although other techniques might be used as well. Figure 2 summarizes the various characteristic shapes of the cyclic voltammetric responses expected for a catalytic reaction of the type shown in Figure 1, in which the rate-determining step (rate constant k) is first order in substrate (bulk concentration: C_A) and catalyst (bulk concentration: C_P). The responses are governed by two (and only two) dimensionless parameters, taken as coordinates of the "kinetic zone diagram" shown in Figure 2.[4,5]

The most familiar situation is that of a large excess of substrate over catalyst (right-hand "no substrate consumption" zone) where the cyclic voltammetric response passes from a reversible "no catalysis" response proportional to the square root of the scan rate to an S-shaped curve independent of the scan rate as the catalytic rate constant increases and/or the scan rate decreases.[6–8] The plateau current density, I_p, is then an easy measure of the rate constant (D_P: catalyst diffusion coefficient):

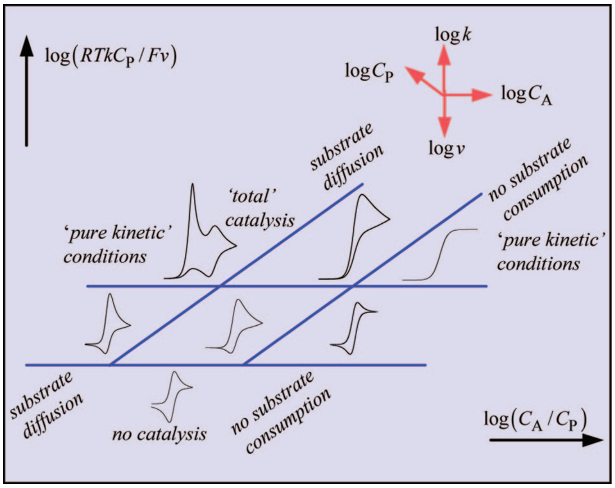


Figure 2. Kinetic zone diagram showing the expected shapes of cyclic voltammetric responses as a function of the two dimensionless parameters taken as coordinates for a catalytic reaction first order in substrate (bulk concentration: C_A) and catalyst (bulk concentration: C_P). v: scan rate.

$$I_p = FC_P\sqrt{D_P}\sqrt{kC_A}$$

The "pure kinetic" conditions thus achieved prevail when the catalytic reaction is fast as compared to diffusion, i.e., when the reaction layer within which the concentration profiles of the catalyst P and Q forms are confined is much thinner than the diffusion layer. At the left-hand end of diagram, consumption of the catalyst increasingly interferes up to the "total catalysis" situation where the first wave of the two-wave system that develops then is governed by the diffusion of the substrate. The peak current density, I_p,

$$I_p = 0.609\sqrt{FC_A}\sqrt{\frac{Fv}{RT}}$$

is no longer a function of the catalytic rate constant, which instead governs the location of the peak potential:

$$E_p = E^0_{P/Q} - 0.409\frac{RT}{F} + \frac{RT}{F}\ln\left(\frac{RT}{F}\frac{kC_P^2}{C_A v}\right)$$

in the cases where the electron transfer between the electrode and the catalyst couple is fast (standard potential: $E^0_{P/Q}$).

How the variations of the experimental concentrations and rate parameters induce the passage from one kinetic situation to the other, in direction and magnitude, is summarized by the red compass rose on top of the diagram.

More complicated kinetic schemes may be encountered in practice as, for example, when two-electron stoichiometries, mixed kinetic control by successive steps, partial deactivation of the catalyst etc. are involved. Several of these schemes are analyzed in ref 9. Any homogeneous catalytic mechanism may be analyzed by "digital simulation"[10] of the cyclic voltammetric responses by means of finite difference resolution of the set of diffusion-reaction partial derivative equations and initial and boundary conditions.[11] Two main commercial packages, Digisim[12] and DigiElech[13] are available for this purpose. In the application of these powerful procedures to reaction schemes involving several successive and/or competing steps, a preliminarily dimensionless analy-

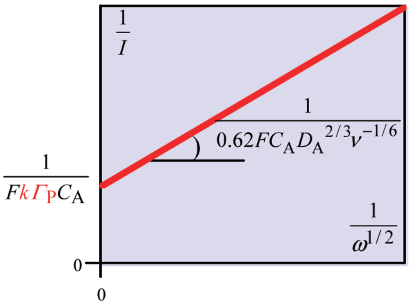


Figure 3. Rotating disk electrode voltammetry of a catalytic reaction first order in substrate and in catalyst at a monolayer coating. “Koutecky−Levich” plot.

sis of the kinetic problem is advisable so as to determine the minimum number of governing dimensionless parameters. This is a necessary step for a lucid assignment of the mechanism and a realistic estimate of grouped rate and equilibrium constants. Examples will be given in section 4.

2.3. Rotating Disk Electrode Voltammetry of Immobilized Catalyst Systems

2.3.1. Monolayers

There are many ways to attach monolayer or multilayered films containing redox centers onto electrode surfaces.[14,15] While cyclic voltammetry and other transient techniques could be used to investigate such systems, rotating disk electrode voltammetry (RDEV) has been mostly used instead.

For monolayer coatings and a catalytic reaction that is first order in substrate and in catalyst, the current density (I)−potential (E) curve is[16]

$$\frac{I}{I_A} = \frac{\dfrac{I_k}{I_A}}{1+\dfrac{I_k}{I_A}+\exp\left[\dfrac{F}{RT}(E-E^0_{P/Q})\right]}$$

which depends on a single dimensionless competition parameter, I_k/I_A, itself defined as the ration of two current densities: $I_k = Fk\Gamma_P C_A$ (Γ_P, total surface concentration of catalyst), which characterizes the catalytic reaction, and $I = FC_A D_A/\delta = 0.62FC_A D_A^{2/3}\nu^{-1/6}\omega^{1/2}$ (δ, thickness of the diffusion layer; ν, kinematic viscosity; ω, rotation rate), which characterizes the mass transport of the substrate.

The two limiting situations reached for I_k/I_A small and large are of the same type as the “pure kinetic” and “total catalysis” conditions, respectively, depicted in section 2.2 for the cyclic voltammetry of homogeneous catalytic systems.

The plateau current density may be expressed as

$$\frac{1}{I_p} = \frac{1}{Fk\Gamma_P C_A} + \frac{1}{0.62FC_A D_A^{2/3}\nu^{-1/6}\omega^{1/2}}$$

giving rise to a “Koutecky−Levich” plot of the variation of the inverse of the current density with the inverse of the square root of the rotation rate (Figure 3), from the intercept of which the catalytic rate constant, k, can be estimated if the surface concentration of the catalyst, Γ_P, is known (if not, $k\Gamma_P$ nevertheless provides an interesting characterization of the catalytic properties of the electrode coating).

2.3.2. Multilayered Films

Expression of the governing parameters by means of characteristic current densities is also worthwhile in the case of multilayered coatings.[17] Besides the catalytic reaction and the diffusion of the substrate in the bathing solution that are characterized by the same current densities as above (Γ_P is now the total amount of catalyst contained in one unit surface area of film, C_A is replaced by κC_A, κ being the partition coefficient of the substrate between the solution and the film), two other rate-limiting factors have to be taken into account, namely, the diffusion of the substrate through the film and electron hopping between the electrode surface and the redox centers in the film, characterized by the current densities, I_S and I_e: $I_S = F_\kappa C_A D_S/d_f$ (d_f, film thickness; D_S, diffusion coefficient of the substrate in the film) and $I_e = FS\Gamma_P D_e/d_f^2$ (D_e, equivalent diffusion coefficient for electron hopping[18–22]).

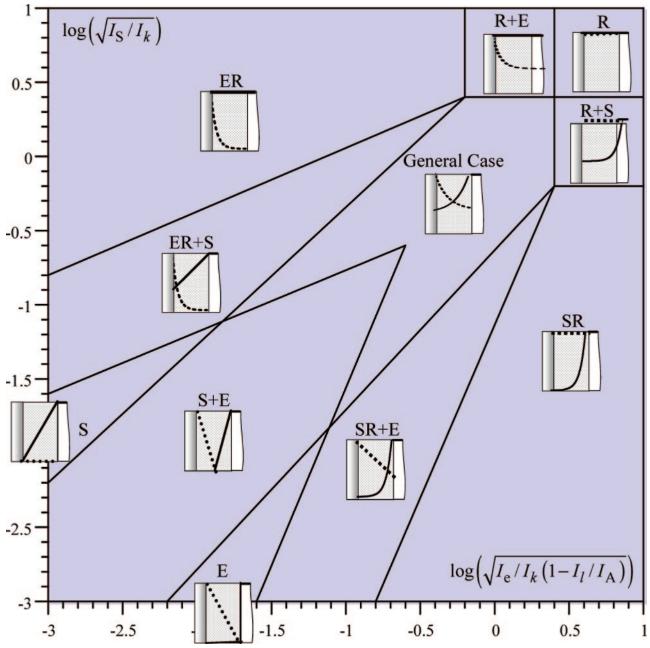


Figure 4. Kinetic zone diagram characterizing the RDEV plateau currents for the reaction scheme in Figure 1. Full lines: substrate concentration profile. Dashed lines: concentration profile of the reduced form of the catalyst. Adapted with permission from Figure 5.5 of ref 26. Copyright 1992 J. Wiley and Sons.

The competition between these rate-limiting factors is represented by the kinetic zone diagram in Figure 4, which corresponds to the simple mechanism depicted in Figure 1.[23–26] The symbolic designation of each zone summarizes the nature of the kinetic control of the current, R for the catalytic reaction, S for substrate diffusion through the film, E for electron propagation. SR and ER apply to fast catalytic reactions and mean a combined control under the pure kinetic mode, in which the catalytic reaction and the diffusion of either the substrate or the electrons compensates each other, giving rise to a thin reaction layer, of thickness $(\sqrt{I_s/I_k})d_f$ and $(\sqrt{I_e/I_k})d_f$. The expressions of the current in each zone of the kinetic zone diagram of Figures 4 are available from Table 4.1 of ref 26. Several more complicated processes have been treated according to the similar approaches. These treatments and the resulting equations are given in the same reference.

The analyses and expressions of the current form the bases on which contemporary rationalization of electrochemical sensors is dealt with, as developed for example in refs 27 and 28.

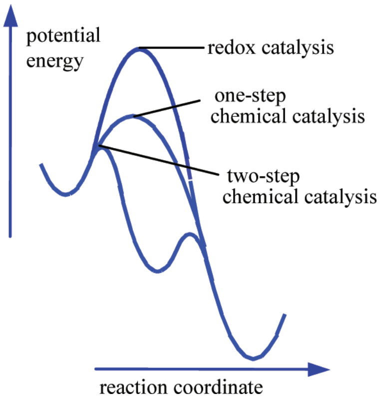


Figure 5. Redox and chemical catalysis. Potential energy profiles.

2.3.3. Rotating Ring−Disk Techniques

Generating a product or an intermediate at a disk electrode and collecting it at a ring electrode that concentrically surrounds the disk is an alternative to cyclic voltammetry. The product or intermediate is generated by fixing the disk potential at an appropriate value and scanning the ring potential so as to obtain its oxidative or reductive signature as a steady-state current−potential curve. This technique has been extensively and successfully applied in the determination of the product, H_2O_2 or H_2O in the catalytic reduction of oxygen (see section 5.3).

3. Contrasting Redox Catalysis with Chemical Catalysis. Carbon−Halogen Bond Reductive Cleavage

3.1. Introduction

As opposed to redox catalysis, where the catalyst acts as an outersphere electron transfer agent, chemical catalysis involves more intimate interactions between the active form of the catalyst and the substrate. A more precise picture of what is meant by "more intimate interactions" leads to distinguishing two situations.

One simply involves bonded interactions in the electron transfer transition state. In other words, electron transfer then possesses an inner-sphere character, which is expected to result in a lower activation energy than for an outersphere electron transfer of same driving force. More stereospecificity is also expected to result from bonded interactions in the transition state. The reduction of vicinal dibromides into the corresponding olefins offers a particularly clear example of this situation both in terms of kinetics and of stereochemistry.

Another situation is when the "more intimate interactions" are so strong that an adduct is formed between the active form of the catalyst and the substrate. The potential energy profiles corresponding to the two situations are sketched in Figure 5. The formation of this intermediate is again expected to be faster than an outersphere electron transfer reaction; the more so the more stable the adduct. A problem that may then arise is the rate of decomposition of the adduct that ensures the formation of the products and the regeneration of the catalyst. Catalysis of the reduction of organic halides by vitamin B12 offers an illustration of this type of chemical catalysis, in relation with the mechanism by which reductive dehalogenases reduce dangerous polyhalide pollutants. We will focus on these two examples taken in the literature on organic halide reduction, noting that several other important reactions pertaining to the same topic are discussed in Anny Jutand's contribution to this issue.

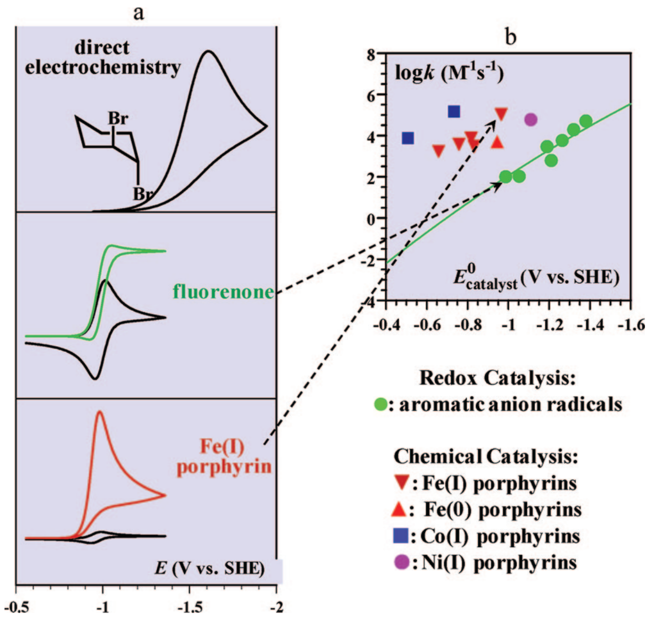
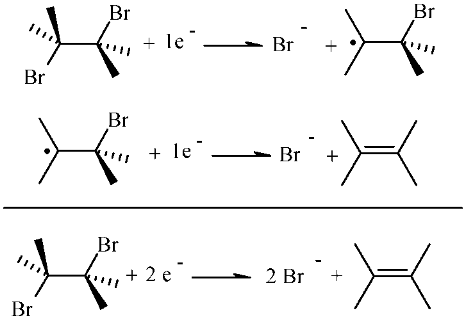


Figure 6. Redox and chemical homogeneous catalysis of *trans*-1,2-dibromocyclohexane. (a) Cyclic voltammetry in dimethylformamide of the direct electrochemical reduction at a glassy carbon electrode (top), of redox catalysis by fluorenone (middle), of chemical catalysis by an iron(I) porphyrin. (b) Catalysis rate constant as a function of the standard potential of the catalyst couple: green dots, aromatic anion radicals; downward brown triangles, Fe(I); upward red triangles, Fe(0); blue squares, Co(I); magenta dots, Ni(I) porphyrins. Adapted with permission from Figures 3 and 4 of ref 36. Copyright 1990 American Chemical Society.

Scheme 2

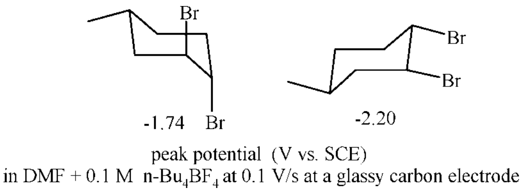


3.2. Kinetics and Stereochemistry of Vicinal Dibromides Reductive Dehalogenation

An early investigation of the *direct electrochemical reduction* of these compounds in an aprotic medium (DMF) showed that the corresponding olefin is formed according to a two-electron stoichiometry (overall reaction in Scheme 2).[29]

Further studies[30−37] revealed that the transfers of the two electrons are not concerted, although the debrominated radical formed in the first step of Scheme 2 is reduced in the second step at a less negative potential than the potential at which the first reaction takes place. The current−potential responses obtained in, e.g., cyclic voltammetry (Figure 6) thus correspond to a two-electron stoichiometry, even though the two electrons come into the molecule successively. Each of the two successive electron transfers is coupled with the

Scheme 3



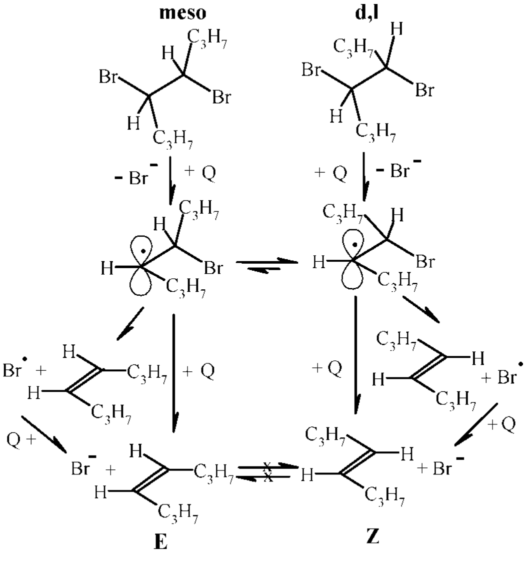
cleavage of a C−Br bond, which occurs concertedly with electron transfer.[34,36] Since both steps are irreversible and the second step is energetically much easier than the first, the overall two-electron process is kinetically controlled by the first step. The reaction is also an example of the role of conformations in electron transfer,[33] in this instance, dissociative electron transfer. There is a clear antiperiplanar preference for the reaction (as illustrated in Scheme 3 in the case of dibromocyclohexane) due to the stabilization of the radical by coupling of the unpaired electron with bromine in the first case. The weaker bond dissociation energy leads to a more favorable standard potential and a weaker intrinsic barrier. When the two conformers are present and can convert one into the other, the reduction follows a "CE" mechanism, which goes through the more reducible of the two.[31,33,34,36]

Since the direct electrochemical reaction is irreversible, it should be possible to catalyze it by redox as well by chemical catalysts. Anion radicals of aromatic molecules are classical homogeneous *redox catalysts* in aprotic media. Catalytic currents are indeed observed when a dibromoalkane is added to a solution containing the aromatic anion radical parent (see the illustrative example of fluorenone in Figure 6).[36] The rate constant of the rate-determining step can be derived from the catalytic increase of the catalyst wave (from the black to the green curve in the fluorenone diagram of Figure 6). The resulting variations of the electron transfer rate constant with the driving force, measured by the standard potential of the catalyst, are shown in the right-hand diagram of Figure 6 (green dots) in the case of *trans*-1,2-dibromocyclohexane. They are in quantitative agreement with the dissociative electron transfer kinetics predicted on the basis of the electrochemical results.[38] Stereochemical studies carried out with *meso* and *d,l* 4,5-dibromooctane showed partial stereoselectivity in the formation of the *E* and *Z* olefin (Scheme 4), thus suggesting the mechanism depicted in the same scheme, where the *E*/*Z* interconversion at the level of the monobromo radical resulting from the first dissociative electron transfer competes with the second electron transfer, leading to an *E*:*Z* ratio different from thermodynamic equilibrium. The redox nature of catalysis is thus attested both by the lack of stereospecificity of the reaction and by the kinetic constraint deriving from the outersphere character of the electron donor. The corresponding activation free energy is indeed given by

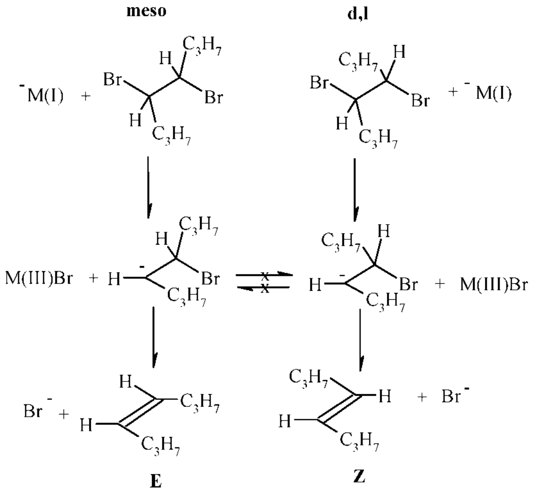
$$\Delta G^{\ddagger} = (\lambda/4)[1 + F(E^{0}_{\mathrm{catalyst}} - E^{0}_{\mathrm{substrate}})/\lambda]^{2}$$

where $E^{0}_{\mathrm{substrate}}$ is the standard potential of the reaction being catalyzed and λ the total reorganization energy that includes, in particular the dissociation of the bond being cleaved concertedly with electron transfer.[39] This equation corresponds to the green line in the right-hand diagram of Figure 6.

Scheme 4



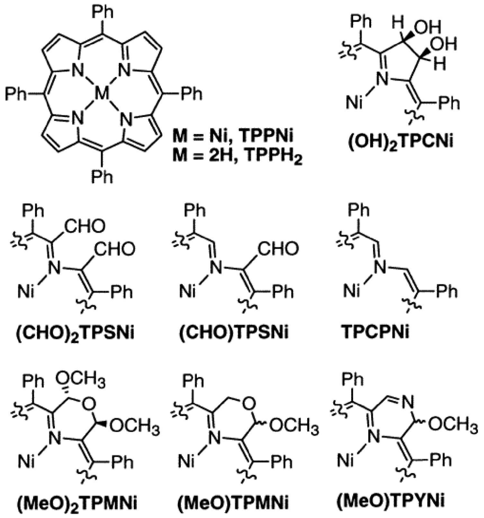
Scheme 5



Catalysis of the reduction of *trans*-1,2-dibromocyclohexane by various Fe(I), Fe(0), Co(I), Ni(I) porphyrins is also represented in Figure 6. Similar results were obtained for other 1,2-dibromides.[36] It clearly appears that, for the same driving force, the rate constants for these catalysts are systematically larger than for the redox catalysts. This kinetic advantage, which reaches several orders of magnitude, points to the conclusion that these various low-valent metalloporphyrins behave as *chemical catalysts*. This conclusion is confirmed by the observation that the reaction is now completely stereoselective, pointing to the mechanism shown in Scheme 5. The Br^+ transfer to the metallic center is followed by an immediate expulsion of the second bromine under the form of Br^-, which is faster than *E*/*Z* interconversion or even concerted with the first step. The same conclusion most likely applies to Co(I) vitamin B12 (Scheme 7), which was shown to react fast ($k \approx 10^7$ M^{-1} s^{-1}) in an aprotic medium at a potential of only −0.5 V vs SHE.[40] The reduction of vicinal dihalides has been used as a test reaction to evaluate the catalytic properties of vitamin B12 in microemulsions, in films deposited on the electrode surface,[41–49] as well as in biphasic systems with vitamin B12 in water and dibromocyclohexane in oil.[50,51]

The observations made with the complexes shown in Scheme 6 as catalysts of the reduction of *trans*-1,2-dibromocyclohexane are also relevant to the distinction between redox and chemical catalysis. As seen earlier, nickel tetraphenylporphyrin (TPPNi) gives rise to chemical cataly-

Scheme 6



sis, while catalysis with the free base (TPPH$_2$) is much less efficient in agreement with the fact that one-electron reduction leads to an anion radical, which behaves as a redox catalyst, with a standard potential that is too positive to produce a significant catalytic efficiency. The Ni(II) homoporphyrins ((MeO)$_2$TPMNi, (HO)TPMNi, (MeO)TPMNi, (MeO)TPYNi) also behave as redox catalysts, in line with the fact that electron injection takes place in the ligand rather than at the nickel. With the Ni(II) chlorin ((OH)$_2$TPCNi), secochlorins ((CHO)$_2$TPSNi, (CHO)TPSNi) and chlorophins (TPCPNi), electron transfer generates a Ni(I) complex, which accordingly gives rise to a more efficient catalysis of the chemical type.

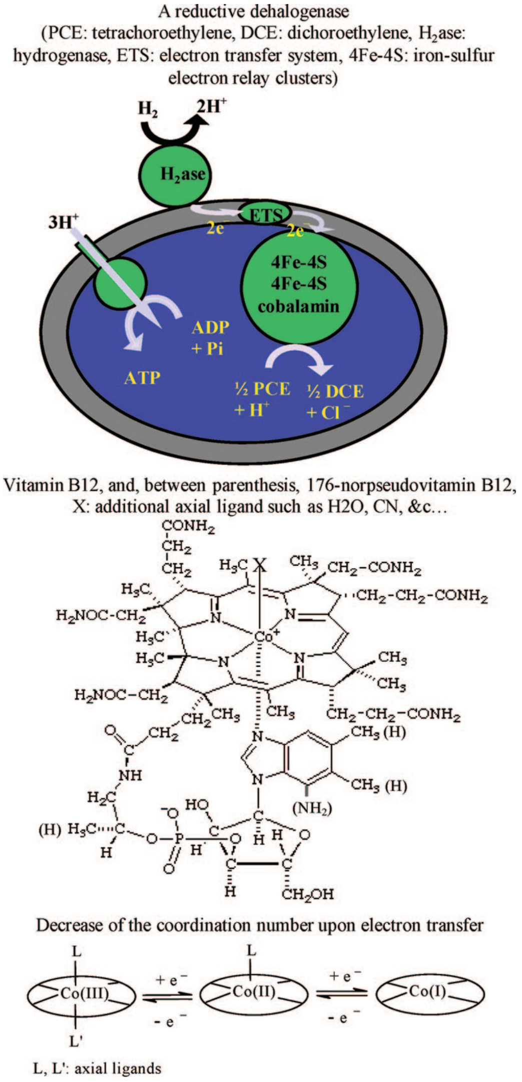
Another example is provided by the C60, C70, C76, C78, and C84 fullerene anions in benzonitrile, which presumably act as redox catalysts.[52–55]

3.3. Vitamin B12 and Reductive Dehalogenases

Low-valent vitamin B12 derivatives, i.e., cobalamin and other cobalt corrinoids (Scheme 7), are involved in the enzymatic reduction of several organic halides, including dangerous polyhalide pollutants, such as tri- and tetrachloroethylene.[56–64] Understanding the mechanism of these enzymatic reactions could be a source of inspiration for depollution strategies. In the enzyme extracted from *Sulfurospirillum multivorans* (formerly *Dehalospirillum multivorans*) norpseudovitamin B12, rather than vitamin B12, serves as the prosthetic group (see Scheme 7),[63] but the redox properties of the two systems should be quite similar at the level of cobalt(I), a level at which catalysis of reductive dehalogenation is expected to take place. Indeed as pictured in Scheme 7, the cobalt(I) complex does not bear any axial ligand, making the difference between vitamin B12 and norpseudovitamin B12 insignificant at the Co(I) oxidation state.

Catalysis of the reduction of chloroacetonitrile by vitamin B12 is a good illustration of a two-step chemical catalysis, facing some difficulty in the regeneration of the catalyst after the initial formation of a catalyst substrate adduct. Monohaloalkanes react readily with Co(I)balamin, sometimes described as a "supernucleophile", in an aprotic medium such as DMF, to form an alkyl−Co(III) complex.[65,66] As shown with *n*-butyl bromide as substrate, this alkyl−Co(III) complex may be further reduced to the alkyl−Co(II) complex, which cleaves, leading to a catalytic process.[67] Catalysis is however very sluggish. Other studies have been performed on the reductive cleavage mechanism of alkyl−cobalt complexes,[68,69] with particular emphasis on the dependence of the redox characteristics of the alkyl complex upon the nature of the axial alkyl ligand.[70] Taking chloroacetonitrile as an example of substrate,[71] Figure 7 shows the catalytic response observed in a protic medium with cobinamide (i.e., vitamin B12 in which the benzimidazole chain has been removed) as catalyst. It appears at the level of the Co(II)/Co(I) wave, between the cobinamide second wave, where the Co(I) complex is generated, and the direct reduction wave of chloroacetonitrile. It consists of two close-spaced irreversible waves, corresponding respectively to the formation and reduction of a new complex resulting from the reaction of the Co(I) cobinamide with chloroacetonitrile. These observations suggest the mechanism depicted in Scheme 8, in which the presence of protons is essential to enforce the decomposition of the alkyl−Co(II) complex, which regenerates the catalyst. The height of the catalytic wave and its peak shape indicate that the catalytic reaction is so fast that the current is governed, at least partially, by the diffusion of the substrate, chloroacetonitrile, toward the electrode surface (see section 2.2 and Figure 2). The essential role of proton donors in the closing of the catalytic loop is confirmed by experiments carried out in a nonprotic medium after addition of an acid.

Scheme 7



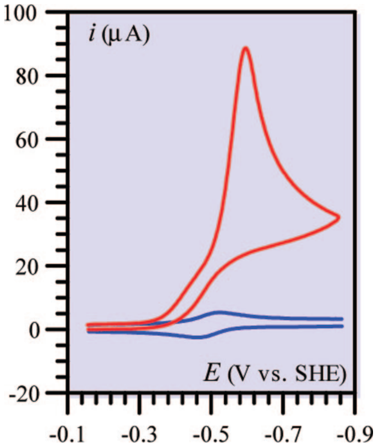
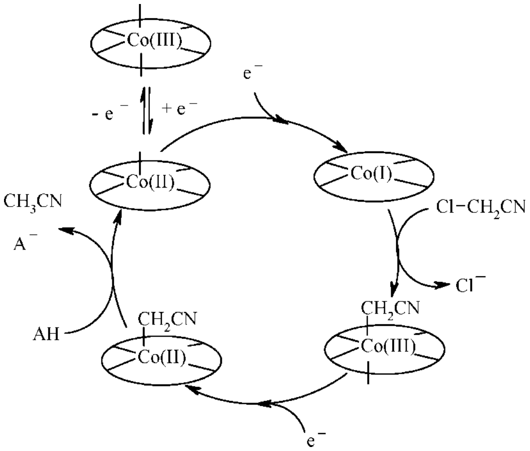


Figure 7. Cyclic voltammetry of cobinamide 0.5 mM alone (blue) and in the presence of 1.5 mM chloroacetonitrile (red) in a 70/30 H_2O−EtOH + 0.1 M NaCl mixture on a glassy carbon electrode at a scan rate of 0.2 V/s. Adapted with permission from Figure 1 in ref 71. Copyright 2005 American Chemical Society.

Scheme 8



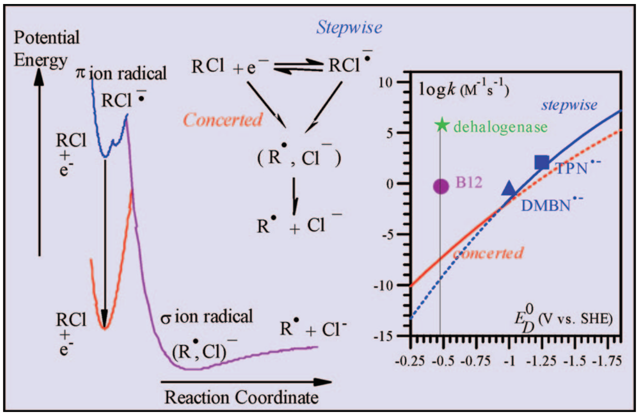


Figure 8. Reductive cleavage of an organic chloride such as tetrachloroethylene, by an outersphere electron donor. Left: potential energy profiles showing the dichotomy and transition between stepwise and concerted electron transfer/bond breaking pathways. Rate constants of the reaction of tetrachloroethylene with the dehalogenase (green star), vitamin B12 (purple dot), and two outersphere electron donors, *viz.*, the anion radicals of 2,4-dimethylnitrobenzene and terephthalonitrile (blue triangle and square, respectively). Lines: activation/driving force plots for the stepwise (blue line) and concerted (red line) electron transfer pathways. Adapted with permission from Figures 1 and 2 in ref 79. Copyright 2005 American Chemical Society.

Scheme 9

$$P \pm e^- \rightleftharpoons Q$$

$$Q + A \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} P + B$$

$$B \xrightarrow{k_c} C$$

$$Q + C \xrightarrow{fast} P + D$$

Another interesting problem is the mechanism by which reductive dehalogenases are able to hydrogenolyze their polychloro substrates. Is an electron transfer mechanism operating, as had been suggested,[72,73] which would mean that vitamin B12 and the prosthetic group of the enzyme function as redox catalysts? The various possible versions, concerted or stepwise, of the initial electron transfer/bond breaking process[74] are sketched in Figure 8, together with the corresponding potential energy profiles. These profiles also take into account the fact that non-negligible interactions may exist between the caged fragments, even in a polar solvent, leading to a σ anion radical rather than to two independent species.[75–78] Taking account of all these factors allows the prediction of the variation of the rate constant for stepwise (blue line) and concerted (red line) electron transfer/bond breaking reaction with the standard potentials of outersphere electron donors, i.e. reagents involved in a redox catalysis process.[79] The validity of these predictions being corroborated by the experimental data obtained with two outersphere electron donors, *viz.*, the anion radicals of dimethylnitrobenzene and terephthalonitrile, it appears that the rate constants for the reaction with the dehalogenase and vitamin B12 are 12 and 7 orders of magnitude above the prediction line, respectively. These results show unambiguously, thanks to the kinetic advantage method, that the reaction with dehalogenase and vitamin B12 are clearly not outersphere electron transfers, but involve more intimate interactions between the reactants, possibly through the intermediacy of organocobalt derivatives.

4. Applications of Homogeneous Redox Catalysis to the Kinetic and Thermodynamic Characterization of Reaction Sequences: Involving Short-Lived Intermediates

In a typical reaction sequence, as the one sketched in Scheme 9, the catalytic increase of the reversible cyclic voltammetric wave of the redox catalyst (mediator) P/Q upon addition of substrate A (see Figure 2 or the middle left-hand diagram in Figure 6 for examples) is a potential source of information on the thermodynamics and kinetics of the first homogeneous electron transfer step ($E^0_{A/B}$, k_e, k_{-e}) and on the rate constant, k_c, for the transformation of the intermediate B.[80] The kinetic control of the system is dictated by the value of the competition parameter $(k_{-e}/k_c)C^0_P$ (C^0_P is the bulk concentration of mediator). When this is small, the initial electron transfer is the rate-determining step. No kinetic information about the follow-up reaction can be gained from the catalytic increase of the current, but it is possible to derive the value of the forward electron transfer rate constant, k_e. The ratio between the catalytic peak current, i_p, and the peak current of the reversible wave, obtained in the absence of substrate, is indeed a function of $RTk_eC^0_P/Fv$ and of C^0_A/C^0_P (v is the scan rate and C^0_A is the substrate bulk concentration). Changing mediator, one can plot the rate constant k_e as a function of the mediator standard potential, $E^0_{P/Q}$ (Figure 9)

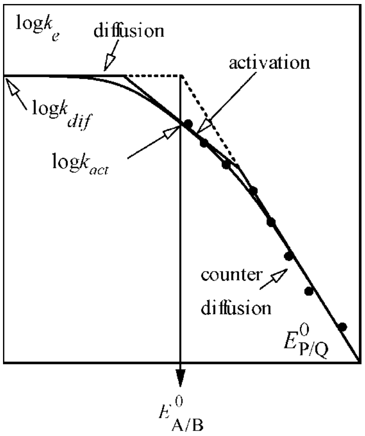


Figure 9. Variation of the electron transfer rate constant with the mediator standard potential. Determination of the standard potential for the formation of an unstable primary intermediate.

and obtain, in addition to the values of k_e, an estimation of $E^0_{A/B}$ as sketched in Figure 9, based on the following equation.

$$\frac{1}{k_e} = \underset{\text{diffusion}}{\frac{1}{k_{dif}}} + \underset{\text{activation}}{\frac{1}{k_{act}}} + \underset{\text{counter-diffusion}}{\frac{1}{k_{dif}\exp\left[\frac{F}{RT}(E^0_{A/B} - E^0_{P/Q})\right]}}$$

Once the standard potential has been obtained, one can derive the homogeneous standard rate constant for the homogeneous electron transfer, i.e., the rate constant at zero driving force.

When the competition parameter, $(k_{-e}/k_c)C^0_P$, increases, a mixed kinetic control situation is achieved, eventually reaching kinetic control by the follow-up transformation of the unstable intermediate. Exploration of this kinetic zone, varying systematically the mediator and substrate concentrations as well as the scan rate then allows the determination of k_c. One can use, for this purpose, working curves relating the peak or plateau current to dimensionless parameters or "simulate" the whole cyclic voltammogram. In both cases, it is important to start the kinetic analysis by the determining the minimal number of dimensionless parameters that govern the kinetics. This approach not only avoids useless calculations but also greatly helps assigning the rate-limiting steps and the passage from one situation to the other upon varying the experimental parameters. Characterization of intermediates down to the nanosecond lifetime can thus be achieved. An example of the possibilities thus offered is shown in Figure 10. It concerns the oxidative deprotonation of methylacridan, a NADH synthetic analogue (see Table 1), by a series of buffers of increasing pH.[113] Comparison with the results obtained with direct electrochemistry at ultramicroelectrodes and with flash photolysis allows a mutual validation of the three techniques.

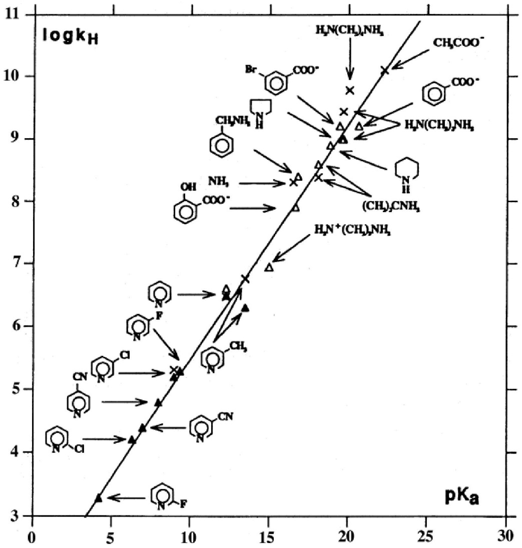


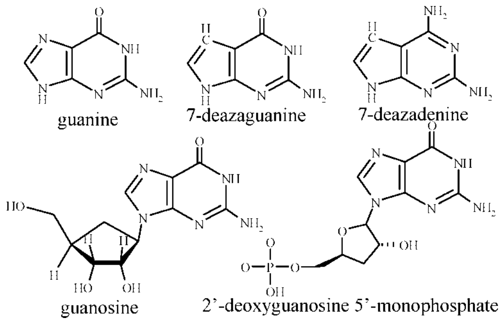
Figure 10. Comparison of high-scan rate ultramicroelectrode cyclic voltammetry (▲), redox catalysis (△) and laser flash photolysis (×) for the determination of the rate constant of deprotonation of methylacridan cation radical by bases of increasing pK_a. Adapted with permission from Figure 6 in ref 113. Copyright 1991 American Chemical Society.

Table 1. Application of Redox Catalysis to the Kinetic Characterization of Fast Follow-Up Reactions (k_c), Standard Potentials of Couples Involving an Unstable Member (E^0) and Homogenous Electron Transfer Rate Constant (k_e)

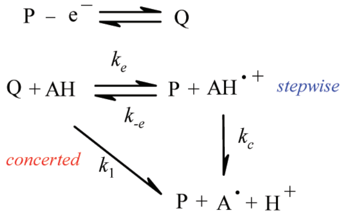
Reaction	medium	k_c	E^0	k_e	ref.
Slow electron transfer conformational changes					
Reduction of *t*-nitrobutane [a]	MeCN	-	-	+	81
Reduction of bianthrone [a]	PhCN	+	+	+	82,83,84
oxidation of 1,4-Bis(dialkylamino)-1,3-butadiene [a]	MeCN	-	+	+	85
Assoc. and dissoc. electron-transfer in Rh hydro-tris(pyrazolylborate) [b]	CH_2Cl_2	+	+	+	86
Reductive cleavage [a]					
aromatic halides	DMF	- + -	+ + -	+ + +	87, 88 89, 90, 91, 92 93
benzyl chloride	DMF	+	+	+	94
fluoromethylarenes	DMF liq NH_3	+	+	+	95
bromo esters	DMF	+	+	+	96
bromothiazole	MeCN	+	+	+	97
halopyrimidines	MeCN	+	+	+	98
1,1-dinitrocyclohexane, α-substituted nitro-alkanes	DMF	+ +	+ +	+ +	99 100
Aromatic epoxides	DMF	-	+	+	101
p-toluenesulfonamides	DMF	-	+	+	102
sulfilimines	DMF	-	+	+	103
di-t-butyl peroxide	DMF MeCN	-	+	+	104
triphenylmethyl-p-nitrophenyl sulfide triphenylmethyl phenyl sulfide triphenylmethyl p-cyanophenyl sulfide	DMF	-	+	+	105 106 107
hexaarylbiimidazoles	MeCN	+	+	+	108
Oxidative cleavage					
C-C cleavage in NADH analogs [c]	MeCN	+	+	+	109, 110
oxalate [d]	water	+	+	+	111
Oxidative deprotonation					
NADH analogs [c]	MeCN	+	+	+	112, 113, 114,115 116, 117, 118
xanthene [a] terpinenes [a]	MeCN	+	+	+	119, 120
N-amidoimidates [a]	MeCN	+	+	+	121, 122
guanine and other cpds in Scheme 8 [d]	water MeCN PEG [e]	-	-	+	123, 124, 125
guanine in DNA [d]	water	-	-	+	126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147
tyrosine	water	+	+	+	148

Mediators: a: aromatic molecules. b: $[Pd\{S_2C_2(CN)_2\}_2]^{2-}$, ferrocene, or ferrocenylacetonitrile. c : substituted ferrocenes. d: coordinatively saturated transition metal complexes. e: polyethyleneglycol

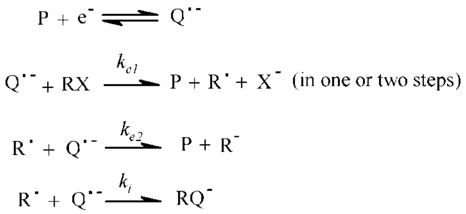
Scheme 10



Scheme 11



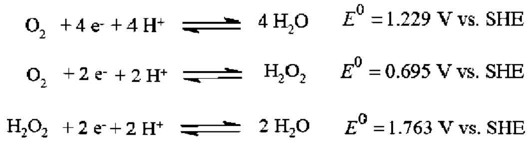
Scheme 12



We have gathered in Table 1 examples of application of redox catalysis to a large variety of processes. They mostly, but nonexclusively, concern organic reactions. For reactions taking place in non-aqueous media, aromatic molecules, giving rise to anion or cation radicals, stable within the time-scale of the experiment, are commonly used as mediators. Ferrocene and substituted ferrocenes are common mediators for oxidation reactions, but also trisbipyridine complexes and other coordinatively saturated transition metal complexes. A long series of papers dealing with oxidative deprotonation of guanine and related molecules (Scheme 10) are worth special attention since it has found sustained application in the interrogation of various forms of DNA (see Table 1) by means of redox catalysis of the guanine they contain. In the original papers, the process under observation is termed "electrocatalytic" but is in fact relevant to the definition of redox catalysis in section 1. The oxidative deprotonation of isolated guanine and derivatives (Scheme 10) has been investigated by means of both redox catalysis and stopped flow kinetics.[123–125] Two mechanisms were envisaged, a two-step process and a concerted process as sketched in Scheme 11 (the proton acceptor may be the solvent or the basic form of the buffer, if present). No systematic kinetic analysis of the type advocated above was carried out, leading to some uncertainty in the mechanism assignment. The same is true for the oxidative deprotonation of tyrosine,[148] a mimic of a similar reaction occurring in photosystem II (see section 6.2), whose mechanisms are still under discussion[148–154] (for more details on proton-coupled electron transfer, and, particularly, its concerted version, see the contribution of Cyrille Costentin in this issue).

Although more restricted in scope, another application of redox catalysis is the *determination of the reduction potential of transient radicals*.[155] Taking the example of a reduction, the reduced form, $Q^{\bullet-}$, of a reversible redox couple, P/Q^{-}, ($Q^{\bullet-}$ is usually an aromatic anion radical in a nonacidic solvent) serves as mediator of the electrochemical reduction of the radical generating substrate, RX, according to Scheme 12. The radical $R^{\bullet}$ thus generated reacts with the redox catalyst, $Q^{\bullet-}$, according to two competing ways. One is the electron transfer reaction of interest. It regenerates P and thus gives rise to the classical catalytic increase of the current. The other is a radical−radical coupling reaction leading to the addition product, RQ^{-}, which deters the catalytic increase of the current. The electrochemical response is therefore a reflection of this competition. Using an appropriate series of mediators, one obtains a "polarogram" of the radical, the half-wave potential of which provides a "reduction potential" from which a true standard potential can be obtained if the rate constants k_i and activation free energy of electron transfer at the half-wave potential are known. These requirements are a drawback of the method as compared to other techniques such as laser flash electron injection[156] and photomodulation.[157]

Scheme 13



5. Reduction of Dioxygen

5.1. Thermodynamics and Direct Electrochemistry

The thermodynamics of O_2 reduction in the presence of proton donors involves the reactions depicted in Scheme 13 together with the corresponding standard potentials.[158] The equilibrium potentials (or apparent standard potentials, E^0_{ap}) are depending on pH in a way that is summarized in Figure 11.

In terms of applications to fuel cells and metal air batteries as well as in the understanding and mimicry of terminal enzymes of the respiratory chain, the four-electron reduction producing directly water is the reaction of main interest as

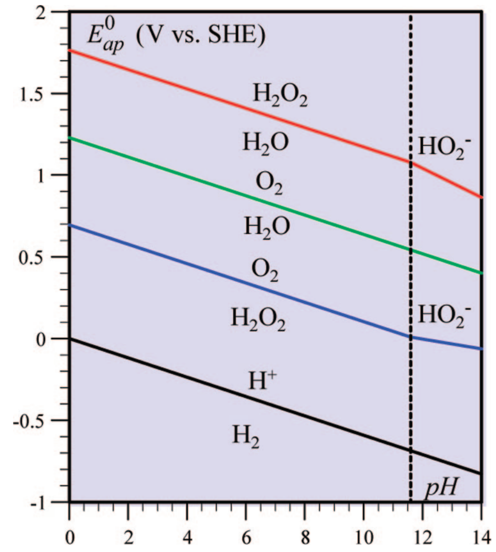
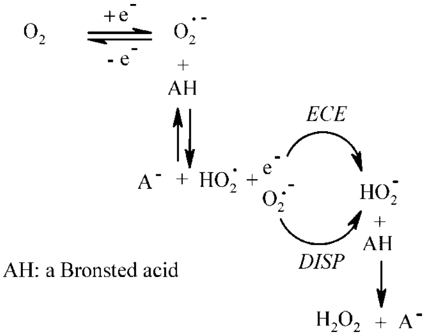


Figure 11. Reduction of oxygen. Apparent standard potentials vs pH.

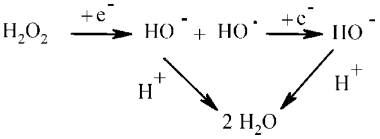
Scheme 14



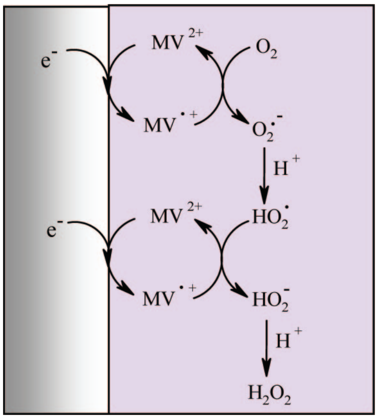
compared to the two-electron reduction that leads to hydrogen peroxide. It is also the most favorable thermodynamically, since over the whole pH domain, H_2O_2 is easier to reduce than O_2. However, in *kinetic* terms, H_2O_2 is more difficult to reduce than O_2 at non-catalytic or poorly catalytic electrodes. This is what has been observed in water on mercury electrodes since the very early days of polarography,[159] and confirmed by further polarographic studies.[160] It seemed likely, from these studies, that the reduction of dioxygen in water is kinetically controlled by the uptake of a first electron, while further electron and proton transfers leads to hydrogen peroxide. The fact that reduction stops at this level implies that H_2O_2 thus produced is kinetically more difficult to reduce than O_2, which is presumably related to the cleavage of the O−O bond. Studies of dioxygen reduction in aprotic solvents, such as dimethylformamide, dimethylsulfoxide or acetonitrile, with progressive addition of proton donors, shed further light on the reduction mechanism. In the absence of proton donors other than residual water, a reversible one-electron cyclic voltammetric wave is observed leading to the paramagnetic superoxide ion radical, $O_2^{\bullet-}$, which is sufficiently stable, even at low scan rate, to ensure the chemical reversibility of the system.[161−163] Depending on the nature of the solvent, and, probably on the amount of residual water, the standard potential of the $O_2/O_2^{\bullet-}$ couple is of the order of −0.6 V vs SHE,[164] considerably negative to the apparent standard potentials of O_2 in water even at the highest pHs. Upon addition of a proton donor, protonation of the superoxide anion radical produces a neutral radical, $HO_2^{\bullet}$, which is much easier to reduce than O_2, thus triggering its reduction at the electrode according to an ECE mechanism[9] and in solution, from $O_2^{\bullet-}$ itself, according to a disproportionation mechanism (Scheme 14).[9] The occurrence of this ECE-DISP process not only entails a two-electron stoichiometry but the addition of the Bronsted acid rapidly leads to kinetic control by the forward electron transfer to O_2.[165,166] This is the combined result of the fact that protonation is fast and electron transfer to O_2 is not intrinsically very fast (the standard rate constant is only 0.03 cm s^{-1} in DMSO). The relative slowness of electron transfer to O_2 is a likely result of the negative charge in $O_2^{\bullet-}$ being concentrated on a fairly small volume, entails a substantial solvent reorganization upon electron transfer and also of the change in bond length when going from O_2 to $O_2^{\bullet-}$, leading to a significant internal reorganization.[166] The result is that the reduction potential, as measured for example by the cyclic voltammetric peak potential at a glassy carbon electrode, very rapidly ceases to shift toward positive values upon addition of acids, even strong acids.

The HO_2^- formed as a result of the ECE-DISP reaction is rapidly protonated by the added acid to give H_2O_2 since the pK of H_2O_2 is much larger than the pK of $HO_2^{\bullet}$.[167] Although not formally proved, the reduction of H_2O_2 most likely occurs by means of a concerted electron transfer bond breaking process[39,168] (Scheme 15) by analogy with what happens with aliphatic organic peroxides.[169] In acetonitrile, in the presence of trifluoroethanol, the cyclic voltammetric peak potential at 0.1 V/s is very negative, −2 V vs NHE. [170]

Scheme 15



Scheme 16



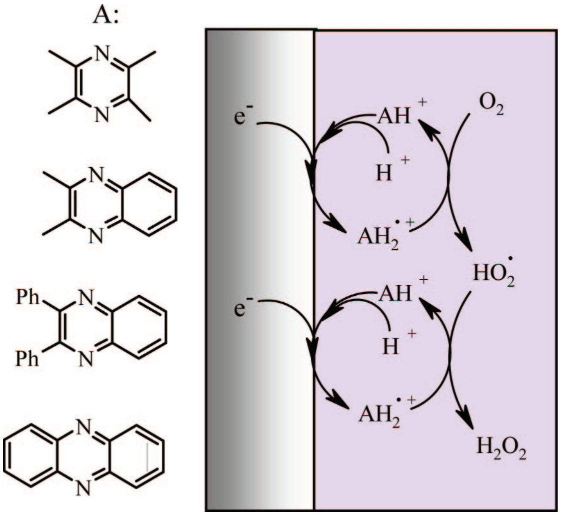
The reduction of O_2 in aprotic solvents, in the presence of weaker, acids such as water or alcohols, disclosed a mode of reduction of $O_2^{\bullet-}$ different from the successive proton electron transfer sequence evoked above: after formation of an H-bond between $O_2^{\bullet-}$ and water, a concerted proton−electron transfer takes place, leading directly to HO_2^- and OH^-.[170−172] At higher water concentrations, the proton moves along 4−5 H_2O chains concertedly with electron transfer.[173]

In view of the kinetic limitations encountered at non-catalytic electrodes, there is plenty room for search for catalysts that would allow a decrease of the over potentials for O_2 and H_2O_2 reduction and possibly favor the four-electron reduction pathway.

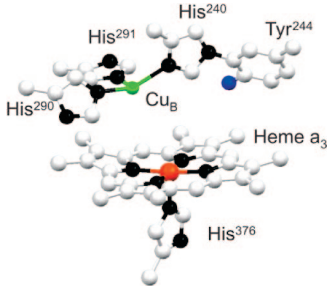
5.2. Redox Catalysis

There have been few attempts to redox catalyze O_2 and H_2O_2 reduction. The best approximation to a redox catalytic system seems to be the $MV^{2+}/MV^{\bullet+}$ couple (MV: methylviologen) in acidic DMSO represented in Scheme 16.[174] The catalytic process is under the kinetic control of the first homogeneous electron transfer. The rate constant of this rate-determining step is compatible with an outersphere electron transfer provided an attraction work term between MV^{2+} and $O_2^{\bullet-}$ is taken into account. This factor enhances to some extent the catalytic efficiency as compared to a purely redox catalytic system. This is presumably the reason that similar systems, *N*,*N′*-dipentyl viologen, and poly(xylylviologen) deposited onto the electrode surface give rise to catalysis.[175,176] In line with its redox, or quasi redox, character catalysis by the $MV^{2+}/MV^{\bullet+}$ couple is not very efficient: catalysis occurs, with a bimolecular rate constant of 2×10^5 M^{-1} s^{-1}, at a potential that is positive to the cyclic voltammetric peak of

Scheme 17



Scheme 18

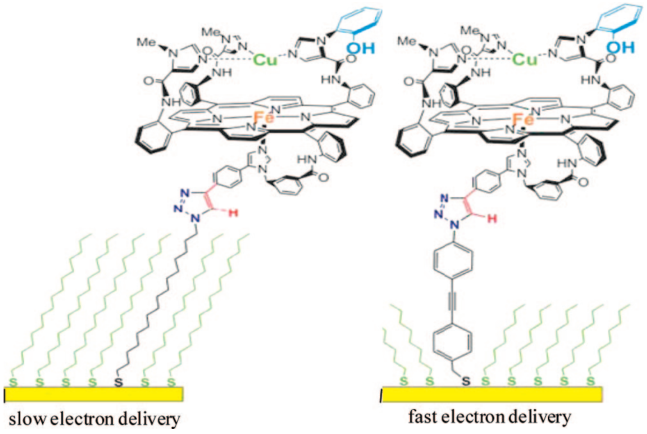


O_2 reduction at 0.1 V/s by only 250 mV. Similar results were obtained with catalysts in the 9-(4-R-phenyl)-*N*-methylacridinium (R = H, Cl, F) series in aqueous solutions and in Nafion gel-modified electrodes.[177] Catalysis of O_2 reduction in acidic 1−4 DMF−water mixtures by the dinitrogen heterocycles shown in Scheme 17[178] bears some resemblance with the above systems, except that the proton used for neutralizing $O_2^{\bullet-}$ or HO_2^- comes from the catalyst itself.

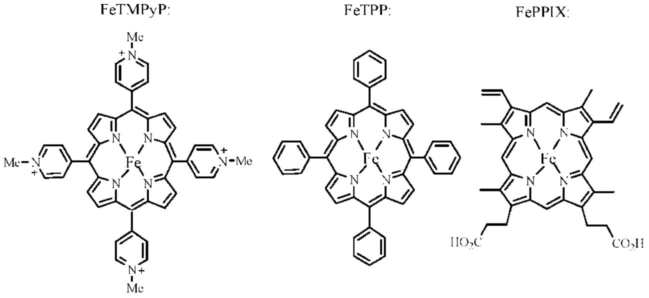
5.3. Chemical Catalysis

As discussed earlier, chemical catalysis often requires the initial formation of an adduct between the active form of the catalyst and the substrate in order to overcome the activation-driving force limitations of outersphere electron transfer. Oxygen transport in hemoglobin and myoglobin has inspired tenacious and successful efforts to synthesize a number of *iron porphyrins* bearing superstructures that sterically protect the oxygen adduct against the formation of μ-oxo and di-μ-oxo dimers and allow the implantation of intramolecular ligands facilitating the formation of the oxygen adduct.[179–182] Addressing O_2 reduction itself, even more remarkable synthetic efforts were made to build molecules that would mimic the active site of cytochrome *c* oxidase. During the final stage of respiration, cytochrome *c* oxidase catalyzes the four-electron reduction of O_2 to H_2O[183–189] to power its proton pump activity.[190,191] The four-electron reduction is essential to avoid the production of toxic partially reduced oxygen species, such as $O_2^{\bullet-}$, H_2O_2, $OH^{\bullet}$. Two electron relays, a copper complex and a heme, mediate electron transfer between cytochrome *c* and the heme-Cu catalytic site shown in Scheme 18, which contains besides a heme and a copper center, a tyrosine residue (Tyr, His is for histidine) able to transfer one proton and one electron in a coupled, or even simultaneous manner. [192–197]

Scheme 19



Scheme 20



As the fruit of patient efforts, a series of molecules mimicking the heme-Cu arrangement were synthesized, able, under their reduced form, to achieve the four-electron reduction of dioxygen into water[198–212] (see Figure 14 in ref 213). The most elaborated model involving the heme, the copper center and the tyrosine residue[214–216] is shown in Scheme 19 and will be discussed later on.

In spite of some 25 years of active research, the mechanisms of catalysis of O_2 reduction by these molecules as well as by simple iron porphyrins are far from being in general agreement. One of the factors that make mechanism analysis difficult is the fact that the catalytic properties of these systems have been tested in most cases, in water, after adsorption on edge plane pyrolytic graphite electrodes.[217] This strategy[218] is not only related to the insolubility in water of most of the iron porphyrins tested as catalysts of O_2 reduction, but also in view of having a catalyst immobilized on the electrode surface rather than dispersed in the solution, so as to avoid separator problems in possible practical applications. Mechanism assignment is not easy under these conditions. This is the reason that reports on O_2 reduction catalysis by water-soluble iron porphyrins are so precious. Out of a series of pioneering studies in the field,[219,220] the results concerning FeTMPyP (Scheme 20) are particularly interesting.[221]

The outcome of this study is that the iron complexes in solution or in the adsorbed state are more likely to catalyze the 4e reduction than the cobalt complexes, which tend to entail the 2e reduction leading to H_2O_2. However, some more detailed conclusions appear uncertain. For example, it was concluded from the cyclic voltammetric experiments summarized in Figure 12, and more precisely from the variations of the peak current shown in Figure 12B, that 4e catalysis

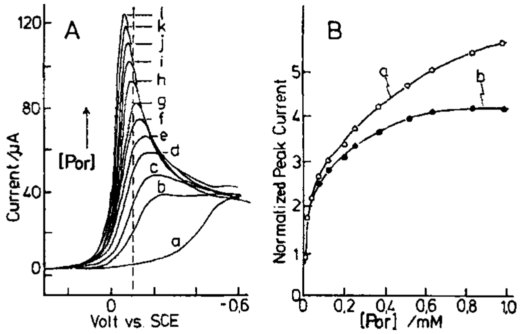


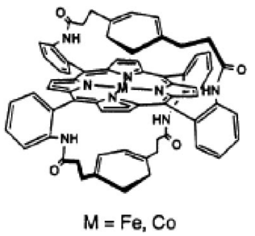
Figure 12. (A) Cathodic part of the cyclic voltammograms for the reduction of O_2 at various concentrations of FeTMPyP: $[O_2] = 0.24$ mM. [FeTMPyP] (mM): curve a, 0.00; b, 0.022; c, 0.044; d, 0.085; e, 0.13; f, 0.20; g, 0.25; h, 0.37; i, 0.51; j, 0.63; k, 0.83; l, 0.99. The broken line indicates the $Fe^{III/II}$TMPyP potential under N_2. (B) Plot of the peak normalized current vs. Fe^{III}TMPyP concentration. Curve a, raw data; curve b; corrected data. Adapted with permission from Figures 2 and 3 in ref 221. Copyright 1983 American Chemical Society.

occurs at high concentrations of the catalyst, whereas the stoichiometry is less at lower catalyst concentrations. It was inferred from this observation that the 4e reaction goes through the intermediacy of H_2O_2, which is further reduced to water by a 2e reaction. In fact these conclusions are uncertain because they were based on the assumption that curves b and c in Figure 12B are a measure of the electron stoichiometry. This would be true if the current response would be controlled by O_2 diffusion all over the catalyst concentration range, corresponding to the "total catalysis" kinetic regime, or close to. This is actually not the case as attested by the change in shape of the voltammograms upon increasing the catalyst concentration, which reflect the passage from a kinetic regime where the catalytic reaction rate governs the current response to a situation where O_2 diffusion is rate-limiting as detailed in section 2.2 and Figure 2 (the effect of scan rate also obeys the predictions of Figure 2). It may thus well be that the 4e stoichiometry is followed over the whole range of catalyst concentrations rendering the 2e + 2e mechanism uncertain.

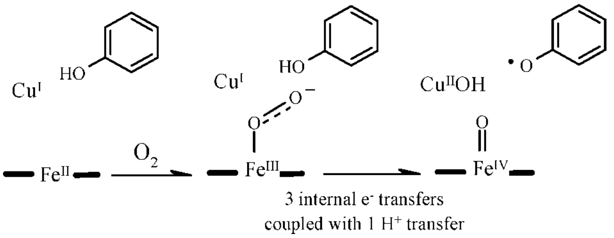
A further investigation of the same iron porphyrin at an edge plane pyrolytic graphite electrode[222] revealed a strong adsorption of the Fe^{II} complex, preferentially to the Fe^{III} complex, which shifts positively the standard potential of the Fe^{III}/Fe^{II} couple by *ca.* 0.2 V. In spite of this positive shift, the adsorbed Fe^{II} complex is a definitely better catalyst than its solution counterpart. Analysis of the Koutecky−Levich plots (see section 2.3) at the plateau of the rotating disk electrode voltammogram indicates 4e stoichiometry. Other studies[218] of this porphyrin, of iron tetraphenyl porphyrin, FeTTP, and of iron protoporphyrinIX, FePPIX (Scheme 20), still adsorbed on edge plane pyrolytic graphite, indicated, by means of rotating ring−disk experiments, the intermediate formation of H_2O_2 and thus of a 2e + 2e mechanism. We may note that in view of the difference in standard potentials, it is conceivable that one mechanism could be operating at the adsorbed state and another one in solution.

There are some indications that dimeric arrangements of adsorbed simple iron porphyrin might be responsible for the prevalence of the direct 4e reduction by analogy with catalysis of oxygen reduction by cofacial cobalt porphyrin dimers (*vide infra*).[223−226] That this would be a general requirement for simple iron porphyrins to catalyze the 4e reduction is however ruled out by the recent finding that an iron porphyrin bearing a superstructure that averts the formation of dimers (Scheme 21) does catalyze the 4e reduction with negligible production of H_2O_2.[206,210]

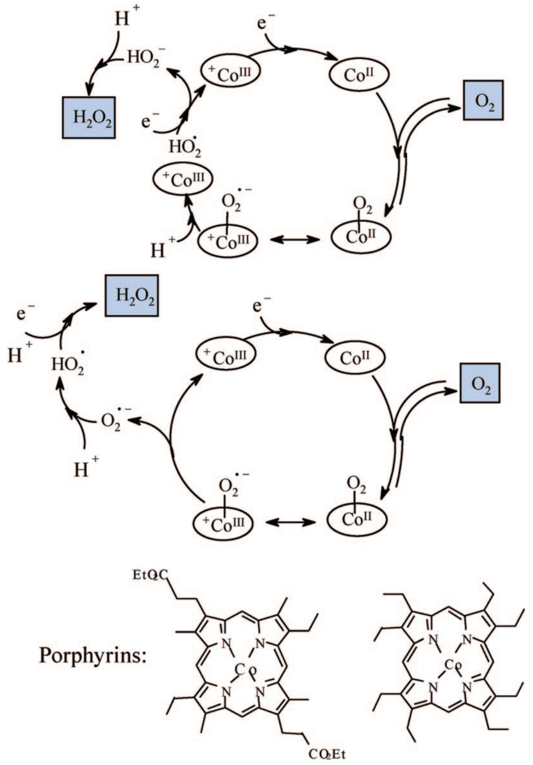
Scheme 21



Scheme 22



Scheme 23



The presence of the copper center and of the tyrosine residue (Schemes 18 and 19) is therefore not strictly essential to catalyze the 4e reduction as long as the electron flux to the system is not limiting as when electrons come from an electrode onto which the system is absorbed. They are, in contrast, required under biological condition according to Scheme 22, as elegantly[215] demonstrated by mimicking the low electron flux and the high electron flux conditions by attaching the system to the electrode by means of a saturated and a conjugated strap, respectively, making use of the thiol self-assembled monolayer technique on gold as represented in Scheme 19. A clear assessment of the role of the copper center and of the tyrosine residue in cytochrome *c* oxidase

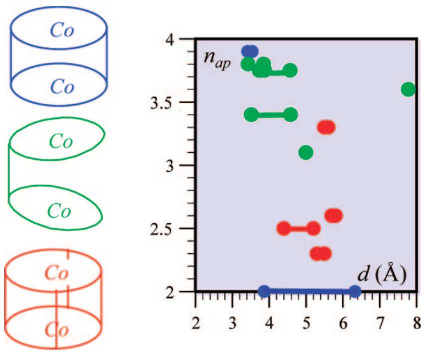


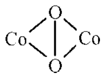
Figure 13. Variations of the apparent number of electrons (n_{ap}) for the catalytic reduction of dioxygen with the distance between the two cobalt porphyrins d, from Table 7 in ref 235.

has thus been reached. Opposite to the iron case, simple cobalt porphyrins have the bad reputation of catalyzing the 2e reduction rather than 4e reduction.[227–232] It is however worth noting that catalysis takes place at a very positive potential (around 0.1 V vs NHE in acidic media). Even only for this reason, it is obviously not of the redox type, in line with the fact that it takes place at a monolayer or within a small number of monolayers. It rather involves, as an essential preliminary step, the formation of a $Co^{II}-O_2$ adduct.[228] This is an uphill reaction as attested by the fact that the peak potential under O_2 is significantly more negative than in the absence of O_2. Two versions of a possible mechanism are as shown in Scheme 23.

The rate-determining step appears to be the formation of the $Co^{II}-O_2$ adduct, which prevents the exact order of the further electron and proton transfer steps, finally leading to H_2O_2, from being disclosed. Similar mechanisms are apparently operating in homogeneous experiments where the cobalt octaethylporphyrin is dissolved in acidic benzonitrile and the electron donor is dimethylferrocene instead of the electrode.[233] In this case the rate-determining step is the uptake of the first electron.

Introduction of cofacial bis-cobalt porphyrins changed drastically the situation since, with structures such as those shown in Figure 13, 4e reduction was observed in a large number of cases depending among other parameters of the cobalt−cobalt distance between the two cobalt porphyrins. As sketched in Figure 8, three types of structures were synthesized and evaluated as catalysts.[234,235] They involve two,[236–246] one[243,247–254] or four straps[255,256] of variable length and structure linking the two cobalt porphyrins. The distance between the two porphyrins is regarded as an important factor in the competition between 4e and 2e reduction.[234,235] Actually, the correlation between the apparent number of electrons and the distance is far from impressive (Figure 13), bearing however in mind that the determination of the distance is rather uncertain. It remains that the cofacial systems may be divided in two groups: one in which the 4e stoichiometry is correlated with the existence of measurable interactions between the two porphyrins in the absence of O_2 another one in which 2e stoichiometry is correlated with the absence of such interactions.

In a number of cases where the 4e reduction prevails, the distance between the porphyrins appears as too short for accommodating another bridging mode of O_2 between the two cobalts other than



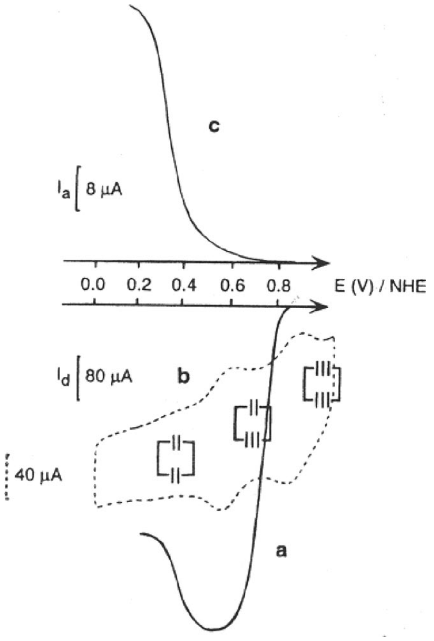
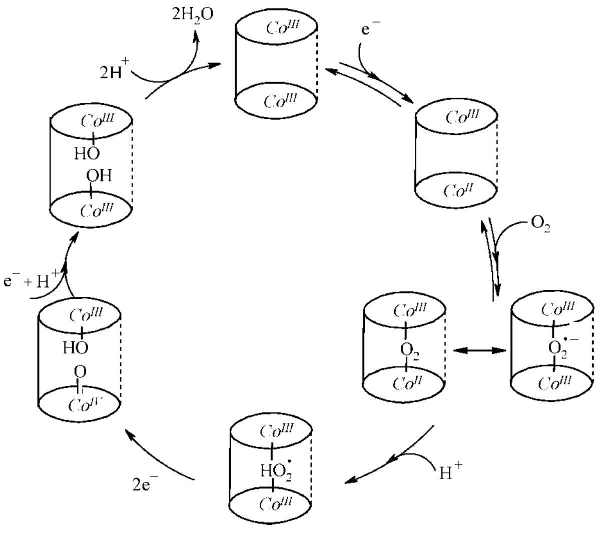


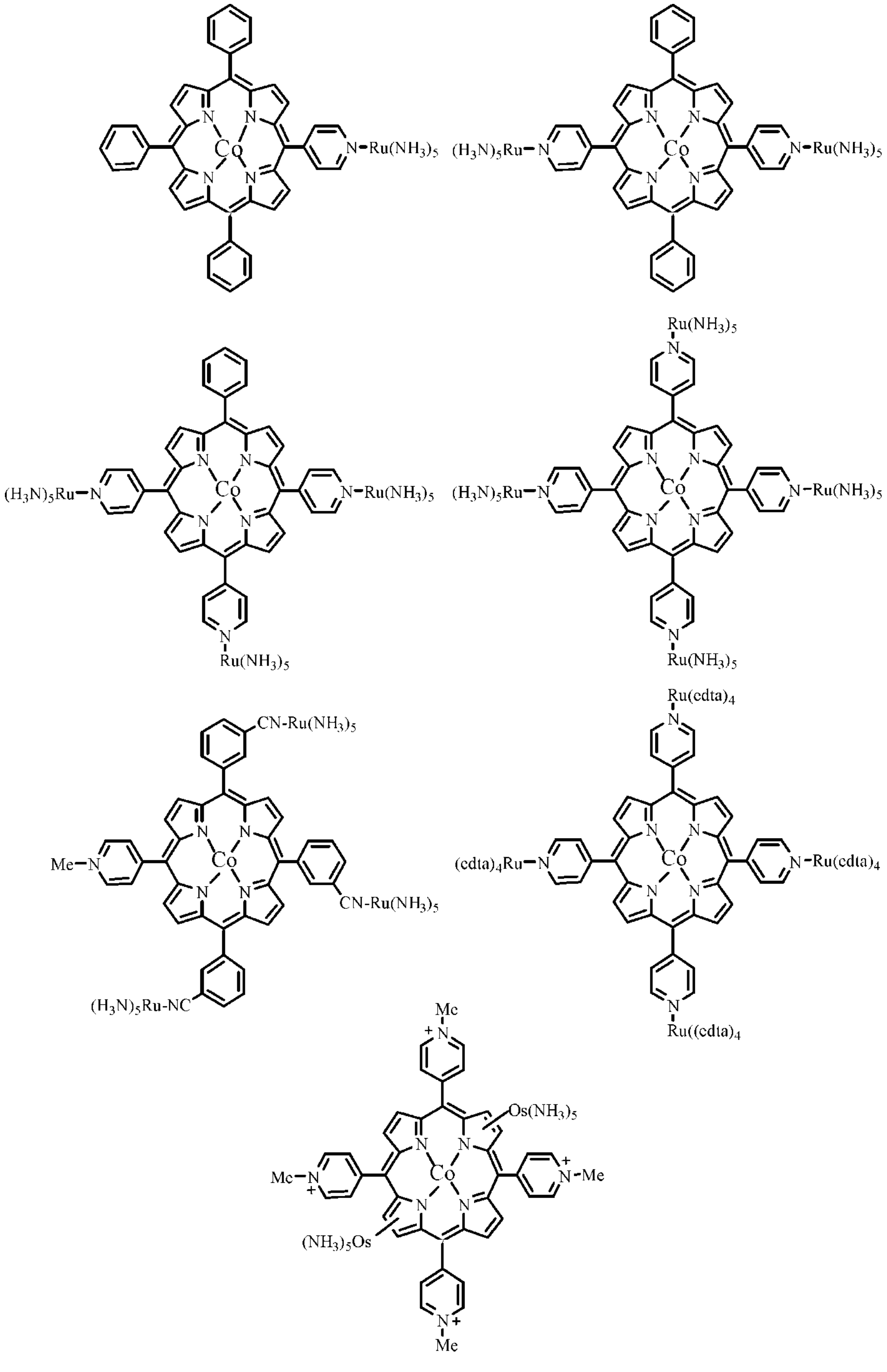
Figure 14. RRDE voltammetry of a 0.5 M H_2SO_4 O_2-saturated solution with an edge-plane graphite disk where a cofacial bis cobalt porphyrin has been adsorbed and H_2O_2 is detected by its oxidation current at the platinum ring. (a and c) Disk and ring current, respectively, as a function of the potential applied to the disk. (b) Cyclic voltammetry (at 0.1 V/s) at edge-plane graphite disk showing the zone of existence of the Co^{III} and Co^{II} oxidation states. Reprinted with permission from ref 243. Copyright 1995 American Chemical Society.

Scheme 24



The more flexible one-strap (pillared) structures adjust themselves more easily to allow the interaction of the two oxygen atoms with the two cobalts.[250,252] It appears that the form of the cofacial system that is catalytically active toward the 4e reduction is the $Co^{III}-Co^{II}$ dimer rather than the $Co^{II}-Co^{II}$ dimer, as results from RRDE voltammetry experiments (Figure 14).[243] The notion that the Co^{III} center plays the role of a Lewis acid, while the Co^{II} center has a radical character, falls in line with the observation that it can be replaced by other metals or even by the protonated free base.[241,243] There are indications that several other parameters may play an important role in a way that remains to be clarified, making the assignment of a precise mechanism difficult at the present time. For example, it is remarkable

Scheme 25



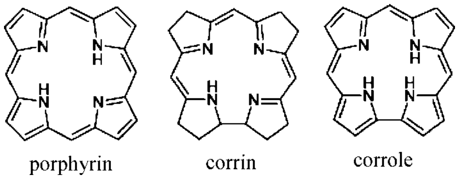
that the mode of attachment to the electrode surface and its nature may drastically change, with the same bis cobalt porphyrin, the competition between the two reduction pathways from a 4e stoichiometry (adsorption on edge-plane graphite) to a 2e stoichiometry (thiol-adsorption on a gold electrode).[246]

The mechanism by which the four protons interfere in the 4e reduction is also difficult to decipher, particularly the question of whether or not addition of one proton precedes the cleavage of the O—O bond in the catalytic cycle. This seems to be indeed the case, assuming that the O—O cleavage is irreversible (which is not granted), with a pillared cofacial bis cobalt porphyrin in acidic benzonitrile (Scheme 24).[233] More indirect arguments led to the same conclusion for a similar pillared system adsorbed on edge-plane graphite.[132] In total, the mechanism of 4e reduction depicted in Scheme 24 does not seem inconsistent with what is known experimentally and computationally at present.

There also several indications that electronic effects created by substituents of the porphyrin ring may exert a profound influence on the 4e/2e dichotomy.[250]

Another important aspect of the same question needs to be discussed: does the prevalence of the 4e reduction require a cofacial bimetallic system or simply appropriately substituted cobalt single porphyrins in spite of already mentioned observation that the 2e reduction seems to be the most common pathway? The answer was given by examination of the catalytic properties of the cobalt single porphyrins shown in Scheme 25.[257–261] At first sight, the four-electron stoichiometry observed with the ruthenium or osmium

Scheme 26



substituted cobalt porphyrins might have been related to the four electroactive substituents. This is actually not the case, if only because of the reduction of the cobalt center by electrons from the electrode. In fact, the metallic substituents exert an electronic effect, via back bonding. More conventional electron-donating substituents, such as OH, in the para-positions of the four phenyl rings of tetraphenylporphyrin give rise to a similar effect.

Although much less frequently, porphyrins of other metals have been used successfully to promote catalysis of the four-electron reduction. This is the case for the iridium(III)/iridium(II) couple with octaethylporphyrin as equatorial ligand, where axial ligation has been found important to ensure a proper binding of O_2 with iridium(II).[262,263] Catalysis takes place at a quite positive potential, *ca.* 0.8 V vs SHE. Iron and cobalt corroles (Scheme 26), both simple and cofacial bis corroles, have attracted active recent attention as catalysts of O_2 reduction. These studies and their results parallel those concerning the corresponding porphyrins.[264–266]

Metal phthalocyanins have also been shown to catalyze O_2 reduction, with a similar 4e/2e dichotomy as with the porphyrins.[220,267] Recent research in this area did not benefit from the sustained attraction, related to biomimetic studies, enjoyed by the porphyrin field. For recent reviews see refs 268–270.

5.4. Concluding Remarks

Molecular catalysis of oxygen reduction has given rise to a huge number of studies involving the ingenious synthesis of an impressive set of more and more sophisticated molecules. These remarkable synthetic efforts have accompanied an increasing emphasis put on biomimetic approaches of the 4e reduction, mostly centered on the imitation and understanding of cytochrome *c* oxidase. In spite of this huge amount of effort, a detailed account of the mechanism that leads to the direct 4e reduction into water and of the parameters that govern its competition with the 2e reduction into hydrogen peroxide is still lacking. Important questions are not completely answered, such as: at what stage does the cleavage of the O−O bond occur; what is the proton/electron transfer sequence. Another source of concern regards the stability of the catalyst toward intermediates such as H_2O_2, $O_2^{\bullet-}$ and, above all $OH^\bullet$. A limiting factor of progress in that direction is the discretion about the effective number, sometimes very small, of catalytic cycles that can be achieved before the death of the catalyst. Unraveling the nature and mechanisms of these deleterious reactions should henceforth be considered as a central issue both for practical and biomimetic purposes.

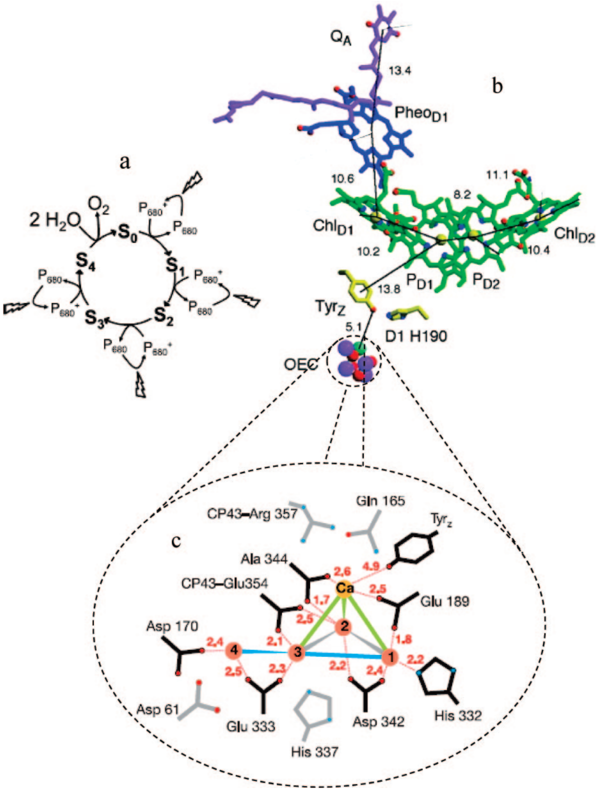


Figure 15. (a) Kok cycle. (b) Structure of the reaction center of photosystem II showing the Tyr_Z-Chl_{D1}(P_{680})-$Pheo_{D1}$-Q_A donor−chromophore−acceptor system, electron transfer from tyrosine (Tyr_Z) being coupled to proton transfer from histidine D1 H190 (the numbers are the distances in Å). OEC: oxygen evolving complex. Reprinted with permission from *Science* (http://www.sciencemag.org), ref 286. Copyright 2004 AAAS. (c) Schematic view of the OEC Mn_4Ca. Reprinted by permission from Macmillan Publishers Ltd: *Nature*, ref 287, copyright 2005. Abbreviations: alanine (Ala), arginine (Arg), aspartate (Asp), glutamate (Glu), and histidine (His). The numbers are the distances in Å. The distances between Mn (red) and Ca (orange), as illustrated by the connecting lines, are as follows: gray, 2.7 Å; blue, 3.3 Å, green, 3.4 Å. In the labeling scheme, amino acids in black are in the first coordination sphere and those beyond in gray.

6. Oxidation of Water. Oxygen Evolution

6.1. Introduction. Thermodynamics, Direct Electrochemistry, Redox Catalysis, Electrocatalysis

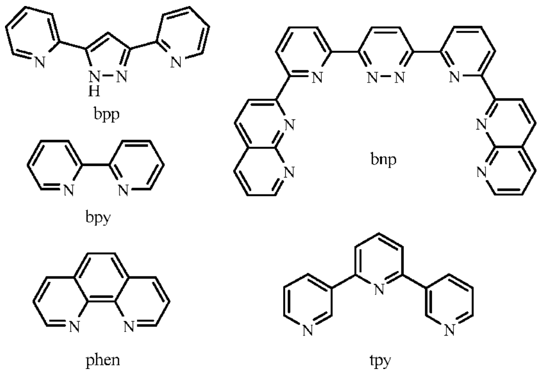
As seen in the Pourbaix diagram of Figure 11, the four-electron oxidation of water into oxygen (Scheme 13) is thermodynamically easier than its oxidation into hydrogen peroxide at all pHs.

Unlike the reverse process of oxygen reduction, an oxidation that would start by an outersphere electron transfer from the water molecule transitorily leading to a cation radical, $H_2O^{\bullet+}$, and then to oxygen by a succession of proton and electron transfers, has never been characterized. The same is true in alkaline media for an electron transfer from OH^- that would lead, in a first step, to $OH^\bullet$. This also applies in the case of an electron transfer that would be concertedly coupled to proton transfer:

$$H_2O - e^- + B^- \rightarrow BH + HO^\bullet \rightarrow \rightarrow O_2$$

In other words, there is no clearly identified electrode material, even carbon,[271] that would simply play the role of

Scheme 27. Polypyridyl Ligands



an electron sink without participating chemically in the reaction.[272] In the potential range where water is oxidized, the metal surface is covered with oxides. Conducting oxide electrodes have thus been systematically investigated as electrocatalytic electrodes.[272–274] The performances of the various electrode materials as anodes in the economically important process of water electrolysis are thus not gauged by reference to an uncatalyzed reaction. They are rather evaluated in a relative manner as one being a better catalyst than another or judged by reference to the thermodynamic potential, their performance being then expressed as the achievement of the smallest possible value of the overpotential. In this framework, it is not surprising that no example of redox catalysis of oxygen evolution has been reported. All reported molecular catalysts are thus of the chemical type, involving exclusively transition metal complexes. Essentially, two metals, ruthenium and manganese, have been used, arranged in dimeric configurations in the hope of promoting O−O bond formation.

6.2. Photosystem II as a Source of Inspiration

The search and testing of these ruthenium and manganese complex catalysts have been from the very beginning and are still strongly inspired by photosynthetic natural systems, particularly, photosystem II (PSII). PSII, a homodimeric multisubunit protein−cofactor complex embedded in the thylakoid membrane, initiates oxygenic photosynthesis in plants, algae and cyanobacteria. It uses sunlight to make high-energy chemicals, according to the general equation

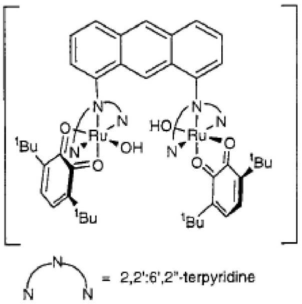
$$CO_2 + 2H_2O \xrightarrow{h\nu} (CH_2O) + O_2 + H_2O$$

where (CH_2O)stands for carbohydrates. The oxygen atoms in the dioxygen molecule come exclusively from the oxidative splitting of water molecules by PSII:

$$2H_2O + 4h\nu \rightarrow O_2 + 4e^- + 4H^+$$

The reaction sequence that takes place at PSII can be summarized as follows.[275–284] Dioxygen is evolved after the sequential absorption of four photons according the Kok cycle (Figure 15a),[285] at the oxygen evolving complex (OEC) as sketched in Figure 15b,c. Each cycle is initiated by sensitization of chlorophyll P680, ChlD1, followed by rapid electron transfer through pheophytin D1 (PheoD1) to the electron accepting quinone QA (Figure 15).[275,286–288] The resulting cation radical, $P_{680}{}^{+}$, oxidizes tyrosine coupled to proton transfer from histidine D1 H190. The resulting tyrosyl radical oxidizes the OEC together with a proton expulsion process that involves the neighboring amino acids. Oxygen evolution takes place after four successive oxidation steps of this type.

Scheme 28



The OEC contains four manganese atoms and a calcium atom arranged as shown in Figure 15c based on crystallographic and spectroscopic data, with μ-oxo bridges between Mn ions. The Mn ions are oxidized within the course of the Kok cycle, and high oxidation states of Mn ions are involved in the water oxidation mechanism.[283,289–291]

Considerable efforts have been made to mimic PSII for the purpose of a better comprehension of its functioning and for designing artificial photosynthetic systems. Roughly speaking, the first goal corresponds to the synthesis, characterization and testing of manganese complexes and the second to those of ruthenium complexes.

Many studies in the field have used electrochemical data under the form of Pourbaix diagrams obtained from cyclic voltammetry or related techniques. In several cases, these complexes have been used as catalysts of the electrochemical oxygen evolution, as discussed in the next sections.

6.3. Ruthenium Complexes

Several dimeric polypyridyl complexes of ruthenium are active as catalysts of oxygen evolution. It appears that an appropriate dimeric framework is indeed favorable, presumably because it serves as template for the formation of the O−O bond. These diruthenium complexes may be divided into two categories according to whether the two ruthenium atoms are directly linked by a μ-oxo bridge or by a sophisticated cage structure serving as template for the formation of the O−O bond.

In the family of *dinuclear complexes with an oxo bridging ligand*, the extensively studied μ-oxo Ru dimer, *cis*,*cis*-$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$ (bpy: see Scheme 27), has been the first to demonstrate an oxygen evolution catalytic activity together with *cis*,*cis*-$[(phen)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(phen)_2]^{4+}$ (phen: see Scheme 27).[292] This result has been confirmed with the same bpy ligands, and elements of the mechanism have been gathered.[293–304] Substituted bipyridine ligands such as 2,2′-bipyridyl-5,5′-dicarboxylic acid[305–307] or 2,2′-bipyridyl-4,4′-dicarboxylic acid[307–309] have also been used showing an improved oxidation rate as compared to the unsubstituted compounds. μ-oxo Ru dimer bpy complexes in which one bpy on one Ru is linked to one bpy on the other Ru by an aliphatic chain, $(-CH_2-)_{2-12}$, have also been shown to be catalytically active.[310]

Similar catalytic properties were observed with complexes of the type $[(tpy)(H_2O)_2Ru^{III}ORu^{III}(OH_2)_2(tpy)]^{4+}$ (tpy: see Scheme 27)[311,312] and also with a trinuclear complex, $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{6+}$.[313]

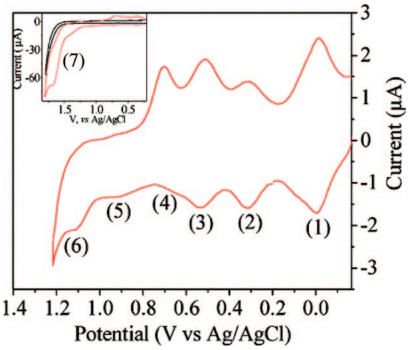


Figure 16. Cyclic voltammograms of [(tpy-PO$_3$H$_2$)(H2O)$_2$-Ru^{III}ORu^{III}(OH$_2$)$_2$(tpy-PO$_3$H$_2$)]$^{4+}$ (red lines) on ITO (Sn(IV)-doped In$_2$O$_3$), in pH 5.0 buffer solution 0.1 M, CH$_3$CO$_2$H/CH$_3$CO$_2$Na) at a scan rate of 40 mV/s vs Ag/AgCl (0.197 V vs NHE). Also shown in the inset is the CV of the ITO background (black line) at the same scan rate. The redox reactions taking place at each of the (1)−(6) waves are summarized in the text. Reprinted with permission from ref 312. Copyright 2007 American Chemical Society.

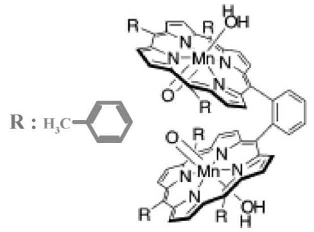
The presence of a μ-oxo bridge between the two rutheniums is not a requisite for catalytic properties as attested by the fact that similar, or even better, catalytic efficiencies were observed with several *dinuclear complexes that do not contain an oxo bridging ligand*, such as [Ru$_2$(bpp)(tpy)$_2$(O)$_2$]$^{3+}$ (tpy, bpp: see Scheme 27),[314,315] [(NH$_3$)$_3$Ru(μ-Cl)$_3$Ru(NH$_3$)$_3$]$^{2+}$,[316] and [RpyRu(bnp)(μ-Cl)RupyR]$^{3+}$ (Rpy: 4-substituted (CH$_3$, CF$_3$, NMe$_2$) pyridine).[317]

An even more efficient catalyst of the same type is the molecule shown in Scheme 28, which contains an anthracene spacer, two tpy ligands and, in addition, two ortho-quinones that also serve as ligands.[318] The efficiency of these molecules as catalysts of O$_2$ evolution has been gauged chemically, rather than electrochemically, in a number of cases, triggering the reaction by addition of a strong oxidant such as Ce^{4+} or Co^{3+} [292,294,296,298–300,303,309,311,314,315,317] and photochemically[306,308] in a few cases. Electrochemical estimation of the catalytic efficiency consisted, in most cases, in measuring the rate of O$_2$ production at a given potential.[293,296,305–307,310,312,313,316] The catalyst is either dispersed in the solution, embedded in a Nafion film[313] or chemically attached to the electrode surface.[312] A rather disparate set of data ensued, from which it is difficult to derive a quantitative comparison between the various catalysts. Cyclic voltammetry has been mostly used to obtain "redox potentials" (in fact, standard or formal potentials) and very rarely to demonstrate catalysis by characteristic high and plateau-shaped waves (see section 2). Two notable exceptions are found in refs 310 and 312. For example Figure 16 reproduces the cyclic voltammetric response of the [(tpy-PO$_3$H$_2$)(H$_2$O)$_2$Ru^{III}ORu^{III}(OH$_2$)$_2$(tpy-PO$_3$H$_2$)]$^{4+}$, where the PO$_3$H$_2$ groups are used to attach the complex to the electrode surface.

The successive waves may be assigned to the following redox couples:
(1) 2e$^-$ Ru^{III}−O−Ru^{III}/Ru^{II}−O−Ru^{II} couple at −0.01 V
(2) Ru^{IV}−O−Ru^{III}/Ru^{III}−O−Ru^{III} at 0.32 V
(3) Ru^{IV}−O−Ru^{IV}/Ru^{IV}−O−Ru^{III} at 0.52 V
(4) Ru^{V}−O−Ru^{IV}/Ru^{IV}−O−Ru^{IV} at 0.68 V
(5) Ru^{V}−O−Ru^{V}/Ru^{V}−O−Ru^{IV} at 0.93 V
(6) Ru^{VI}−O−Ru^{V}/Ru^{V}−O−Ru^{V} at 1.09 V
(7) Ru^{VI}−O−Ru^{VI}/ Ru^{VI}−O−Ru^{V} at *ca.* 1.5 V

It appears that the catalytic couples correspond to waves (5)−(7) and that the catalytic current increases together with the standard potential of the redox couple. Electrochemistry thus allows an easy identification of the active catalysts and provides a rough estimation of the catalytic efficiencies. A more detailed analysis of each catalytic wave would allow the derivation of catalysis rate constants. This approach is clearly simpler than homogeneous kinetic studies with a solution oxidant in which the thermodynamics, and possibly the kinetics of the electron transfer step that precedes the catalytic process should be taken into account in the deciphering of the raw data.

Scheme 29



In spite of a large number of studies, the assignment of the catalytically active species and the mechanism of oxygen evolution remain open to discussion.[302,312,319] One piece of knowledge seems however established: oxygen evolution goes through the intermediate formation of a Ru═O species where the oxidation degree of Ru is at least IV. Deactivation of the catalysts, catalysis being often limited to a few turnovers, seems to be related mainly to anation and bond breaking upon electron transfer.

6.4. Manganese Complexes

In spite of the fact that manganese is the essential ingredient of the oxygen evolution center of PSII, catalysis of water oxidation by artificial manganese complexes has been much less successful than catalysis by ruthenium complexes. In the case of manganese too, two families of dinuclear complexes have been explored, one in which the two manganeses are linked by di-μ-oxo bridges and the other with no μ-oxo bridging between the manganeses.

In the first category, it has been reported that [(bpy)$_2$-Mn(O)$_2$Mn(bpy)$_2$]$^{3+}$ can serve as catalyst in the electrochemical oxidation of water into oxygen when in suspension in water or coated on the electrode surface,[320–322] in contrast with the results of an electrochemical study showing that the dimeric complex is electrochemically oxidized into the tetranuclear complex [Mn$_4$O$_6$(bpy)$_6$]$^{4+}$.[323,324] In the same family of complexes, oxygen is produced by oxidation of *in situ* generated[325] or separately prepared and characterized[326,327] [(tpy)(H$_2$O)$_2$═Mn^{IV}(O)$_2$Mn^{III}(OH$_2$)$_2$(tpy)]$^{3+}$ by KHSO$_5$ or NaClO.[326,328] However the question arose of the origin of the evolving oxygen, water or KHSO$_5$ or NaClO. ^{18}O labeling experiments seemed to indicate that oxygen comes partly from water and partly from KHSO$_5$,[328,329] at variance with other work showing that there is no oxygen evolution when Ce^{4+} is used as oxidant.[330] However, oxygen evolution occurs unexpectedly under the same conditions when Montmorillonite clay is added to the reaction medium.[330,331] The inability of the above dinuclear complex to oxidize water is confirmed by a careful electrochemical study in which it was shown that the dimeric complex [(tpy)(H$_2$O)$_2$Mn^{IV}-(O)$_2$Mn^{III}(OH$_2$)$_2$(tpy)]$^{3+}$ can be obtained by electrochemical oxidative dimerization of the monomer [(Mn^{II}(tpy)$_2$]$^{2+}$ and that its own electrochemical oxidation produces a linear tetramer, [Mn$_4$O$_6$(bpy)$_6$]$^{4+}$, in which the two dimeric units

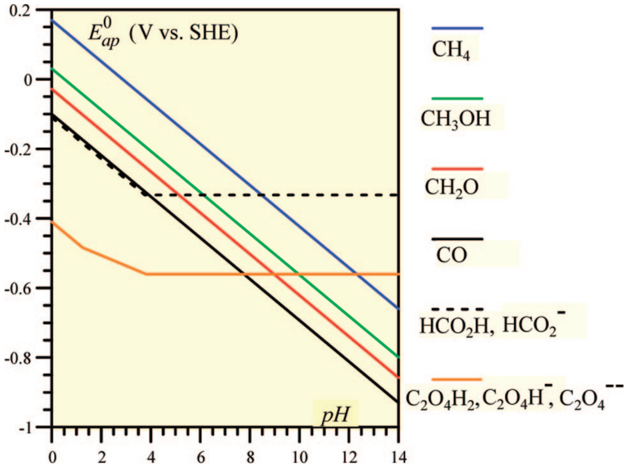


Figure 17. CO_2 reduction. Apparent standard potentials vs pH.

are linked by a μ-oxo bridge,[332] a structure confirmed later on after chemical oxidative dimerization of the dimer.[333] In fact, the discussion on the catalytic properties of the dimer still goes on after the observation that it does catalyze water oxidation by Ce^{4+}, but is deactivated in acid media.[334]

Recent efforts to mimic more closely the OEC have produced and characterized a manganese−oxo "cubane" core complex $Mn_4O_4L_6$ (L: $Ph_2PO_2^-$), which indeed retains some of OEC's properties but not yet the water oxidation capability.[335]

Among dinuclear complexes with no μ-oxo bridging between the manganese atoms, the dimeric molecule shown in Scheme 29, where the two Mn tetraarylporphyrins are linked by a 1,2-phenylene bridge, has been shown to catalyze anodic oxygen evolution in an acetonitrile−water mixture, following a strategy that is reminiscent of the face-to-face cobalt porphyrin approach of oxygen reduction catalysis (see section 5).[336] Chemical oxidation experiments, including with ^{18}O labeling, confirmed that the oxygen does come from the oxidation of water and assign the Mn^V−Mn^V dimer as the catalytically active form.[337]

6.5. Concluding Remarks

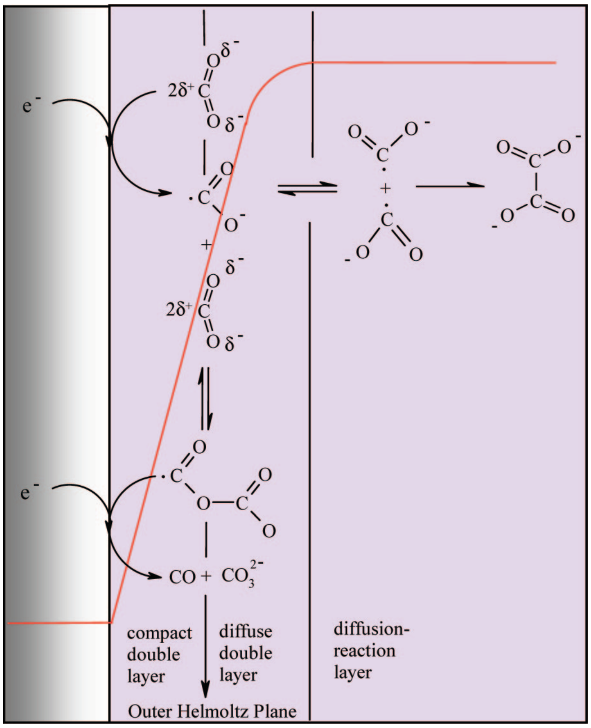
As for oxygen reduction, or even more, the search of molecular catalysts of water oxidation has been and is still inspired by biological systems, mainly photosystem II in this case. In spite of more than twenty years of continuous and still very active ingenuous efforts, we seem still far from satisfactory systems in terms of mimicking Nature or simply in terms of efficient and durable catalysis. The time has probably come for a more systematic comparative evaluation of the catalysis performances and mechanistic analysis of catalysis and deactivation of the catalyst. In this endeavor, an increased recourse to electrochemical kinetic and mechanistic methods should be of help.

7. Reduction of Carbon Dioxide

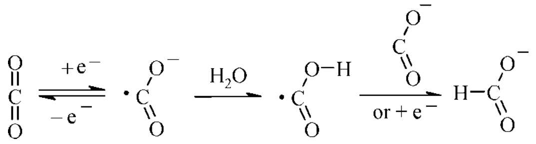
7.1. Introduction. Thermodynamics

CO_2 is the planet's most important source of carbon and one of the most important atmospheric gases contributing to the greenhouse effect. These are the reasons that its electrochemical reduction into fuels attracts sustained attention. Although examples of successful 6-electron and 8-electron conversion into methanol and methane respectively have been described, the most common reduction products are formic acid, carbon monoxide and oxalic acid. Equilibrium potentials in water for a series of CO_2 reductions and their variations with pH are shown in Figure 17.[338]

Scheme 30



Scheme 31



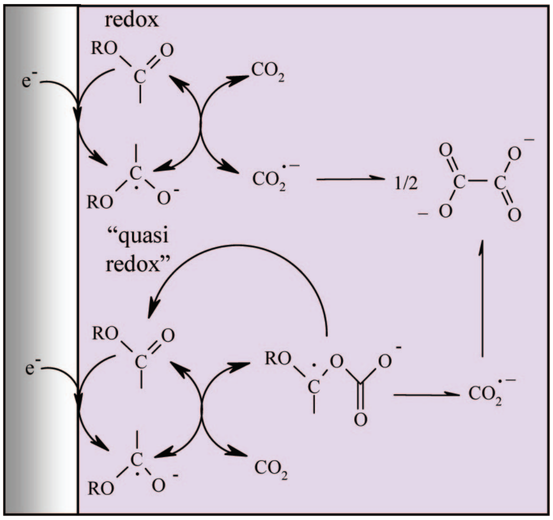
Another interesting piece of thermodynamic information is the standard potential for the formation of the anion radical $CO_2^{\bullet-}$: −1.97 V vs SHE in DMF;[339] −1.90 V vs SHE in water.[340]

The fact that the potential require to produce $CO_2^{\bullet-}$ is so largely negative to the potentials where the products listed in Figure 17 are generated implies large overpotentials in the reduction on inert electrodes and also in reductions mediated by redox catalysts. The latter reactions are nevertheless worth analyzing kinetically and mechanistically since they provide a reference framework for discussing the way in which the chemical catalysts operate.

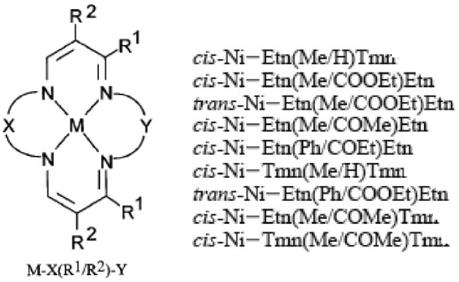
7.2. Electrochemistry at Inert Electrodes

Mercury and lead provide good approximations of inert, "outersphere" electrode materials for CO_2 reduction. From the analysis of the voltammetric responses in DMF[339] and of product distribution in preparative scale electrolysis,[341] the reduction mechanism leading to the three main products, formate, oxalate and carbon monoxide, could be established and the competing pathways kinetically characterized.[342−345] Scheme 30 shows the competition between the CO and formate routes in an aprotic solvent such as DMF in the absence of purposely added water. The dimerization of the anion radical is fast in DMF[339] and in water (from pulse radiolysis experiments[346]), close to the diffusion limit in both

Scheme 32



Scheme 33



cases. Addition of water opens a new pathway that leads to formate, which is obtained by protonation of the anion radical and the uptake of an additional electron from the electrode (ECE route) and/or $CO_2^{\bullet-}$ (DISP route) according to Scheme 31.

In water, formate is the only reduction product.[347]

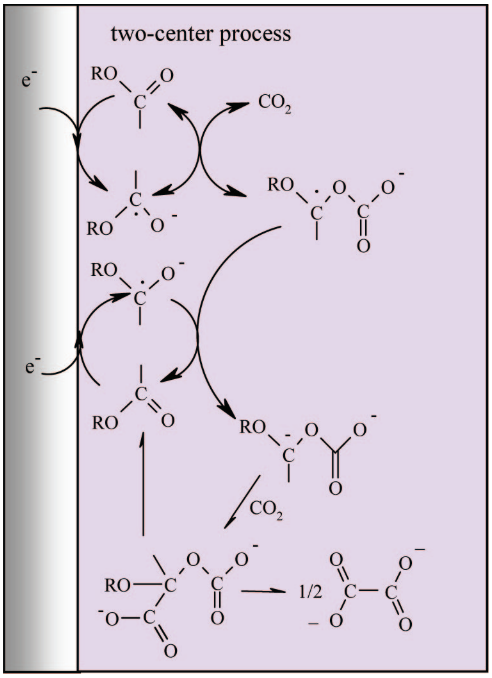
7.3. Electrocatalysis

A very large number of electrode materials, carbon and practically all metals have been tested for the reduction of CO_2 in water. Depending on the electrode material and in competition with hydrogen evolution, higher reduction products such as methanol and methane are formed besides the aforementioned two-electron reduction products.[348] Copper is remarkable in this respect, and the conditions for methane production have been the object of detailed studies.[349] In spite of this large amount of work a clear mechanistic rationale of the relationship between electrode material and products is still missing.

7.4. Redox Catalysis or "Quasi Redox" Catalysis

As exemplified in section 3, anion radicals of aromatic hydrocarbons and substituted aromatic hydrocarbons are classically used as reduction redox catalysis in nonprotic media. This procedure does not apply in the present case since reductive carboxylation takes place, thus rapidly deactivating catalysis. An exception to this rule is provided by aromatic esters and nitriles.[350] In all cases the reduction product is exclusively oxalate. The catalytic efficiency rapidly decreases when the standard potential of the catalyst couple becomes more positive. These observations points to a redox catalysis mechanism in which two anion radicals of CO_2 would couple to give oxalate after being produced by an outersphere electron transfer between CO_2 and the ester or nitrile anion radical (upper reaction scheme in Scheme 32). However a closer examination of the variation of the catalytic rate constant with the reaction driving force measured from the standard potential of the catalyst couple (from −1.67 to −2.04 V vs SHE), points to an inner-sphere character of the electron transfer, implying the transient formation of an adduct as depicted in the "quasi redox" reaction scheme at the bottom of Scheme 32, in which the result of the electron transfer reaction is still $CO_2^{\bullet-}$ as in the purely redox case. In this two-step process, the rate-determining step is the cleavage of the adduct, its formation acting as a pre-equilibrium in the less negative range of catalyst standard potentials and the kinetic control gradually passing to the adduct formation as the standard potential decreases.

Scheme 34



Two families of transition metal complex catalysts also give rise to the exclusive formation of oxalate at potentials that are not far from the standard potential of the $CO_2/CO_2^{\bullet-}$ couple and are thus likely to involve a redox or "quasi redox" catalysis scheme. In a first case, the catalyst is the one-electron reduced form of Ag^{II} and Pd^{II} porphyrins, presumably anion radicals of the Ag^{II} and Pd^{II} complexes, rather than Ag^{I} and Pd^{I} porphyrins.[351] The other family consists of the nickel macrocycles shown in Scheme 33.[352] The cyclic voltammetric results point to a redox or "quasi redox" catalysis scheme in which electron transfer acts as a pre-equilibrium to a rate-determining dimerization. The fact that a measurable rate constant is obtained only for catalysts whose standard potential is close to the direct electrochemical reduction of CO_2 falls in line with the redox character of the catalytic process. As seen in the next section, another family of catalysts, whose standard potentials are much less negative, also gives rise to the exclusive formation of oxalate. Redox catalysis is thus excluded in this case, and a two-center reaction is deemed to operate. This possibility, depicted in Scheme 34, cannot be ruled out in the aforementioned case of aromatic esters and nitriles, since the

Table 2. Transition Metal Complex Catalysts of CO_2 Reduction

Complex	Products	E^a	Medium	Ref.
Polypyridyl Rhenium Complexes (the ligands are shown in Schemes 27 and 35.)				
Homogeneous catalysis				
fac-Re(bpy)$(CO)_3Cl$	CO CO	-1.3, -1.5 -1.25	MeCN, DMF 9-1 DMF-H_2O	353 354
fac-Re(dmbpy)$(CO)_3Cl$	CO	-	MeCN	355 356
fac-Re(ptpy)$(CO)_3Cl$	CO	-	DMSO	357
Re(bpy)$(CO)_3L$ L:Cl^-, $CF_3SO_3^-$, MeCN, $P(OEt)_3$) Re(dmbpy)$(CO)_3L$	CO HCO_2^-	-	MeCN, THF	358
Re(bpy)$(CO)_3$(py)	CO		MeCN synergistic effect of weak Bronsted acids	359
Supported catalysis. Polymer films				
fac-Re(vbpy)$(CO)_3L$ L: Cl^-, MeCN electropolymerized or copolymerized with: *cis*-Ru$(bpy)_2(vpy)_2$	$(CO_2)_2^{2-}$ CO CO	-1.3	MeCN	360 361 362
fac-Re(vbpy)$(CO)_3Cl$ electropolymerized onto meso-porous TiO2 electrodes	CO	-	MeCN	363
Re(pyrrolbpy)$(CO)_3Cl$ electropolymerized	CO	-1.6	MeCN	364 365 366
Re(bpy)$(CO)_3Br$ Re(tpy)$(CO)_3Br$ in Nafion	CO HCO_2H H_2	-1.0, -1.4	H_2O	367
Physical chemistry, uv-vis, esr spectroelectrochemistry with no CO_2				
Re(bpy)$(CO)_2\{P(OEt)_3\}$				368
Re(bpy)$(CO)_3Cl$;Re(dpp)$(CO)_3Cl$ $\{Re(CO)_3Cl\}_2$(dpp)			MeCN,DMF CH_2Cl_2	369
ReL$(CO)_3L'$; L: bpy, i-Pr-PyCa, dapa, dpp, abpy; L': Cl^-,Br^-,I^-,$SO_3CF_3^-$,THF,MeCN,n-PrCN,PPh_3,$P(OMe)_3$			-	370
Re(bpy)$(CO)_3X$, X: Cl^-, $CF_3SO_3^-$, CH_3O^-, H^-, THF, CH_3CN, CO, HCO_2^-, HCO_3^- and $CH_3C(O)^-$			-	371
Other Polypyridyl Metal Complexes (the ligands are shown in Schemes 27 and 35)				
Homogeneous catalysis				
Ru$(bpy)_2(CO)_2$ Ru$(bpy)_2$(CO)Cl	CO HCO_2^- H_2	-1.25	1-1 DMF-H_2O	372 373 374 375
Ru$(bpy)_2$(CO)H	CO HCO_2^-	-1.35	MeCN+H_2O	376
Ru(dmbbbpy)$(bpy)_2$ [Ru(dmbbbpy)$(bpy)_2]_2$	$(CO_2)_2^{2-}$ HCO_2^-	-1.26 -1.36	MeCN MeCN+H_2O	377
[Ru$(bpy)_2$(dpq)$]_2IrCl_2$ [Ru$(bpy)_2$(dpb)$]_2IrCl_2$	HCO_2^-	-1.51, -1.41	MeCN	378
Ru$(bpy)_2(CO)_2$	CO HCO_2^-	-1.46	8-2 EtOH-H_2O at -20°C	379 380 381 382 383
Ru(bpy)(tpy)(CO)	CO HCO_2^- HCHO CH_3OH $H(O)CCO_2^-$ $HOCH_2CO_2^-$			
Ru$(bpy)_2$(qu)(CO) Ru(bpy)$(napy)_2(CO)_2$	CH_3COCH_3	-1.31	DMSO +$(CH_3)_4N^+$	384 385 386 387
cis-Rh(bpy)$(O_3SCF_3)_2$	HCO_2^-	-1.05	MeCN+H_2O	388 389
Os$(bpy)_2$(CO)H	CO HCO_2^-	-1.15 -1.45	MeCN+H_2O	390 391
Rh(η-Me_5C_5)(bpy)Cl	HCO_2^-	-1.3	MeCN+H_2O	392
Rh$(L)_2Br_2$, Ir$(L)_2Cl_2$ L: bmp, dpr, dpq, dpb	HCO_2^-	-0.9	MeCN	393
Ru(dmbbbpy)$(bpy)_2$ [Ru(dmbbbpy)$(bpy)_2]_2$	$(CO_2)_2^{2-}$ HCO_2^-	-1.26 -1.36	MeCN MeCN+H_2O	394
Ni$(bpy)_3$	CO	-1.0	MeCN	395
Co, Fe, Ni, Cu $(phen)_3$	CO HCO_2^-	-	DMSO	396
Co(qpy)$(OH_2)_2$ Ni(qpy)$(MeCN)_2$	CO	-1.45	MeCN	397
Co, Fe, Ni, L_2 L: dapa, tppz,tptz, tpen,tpy, vtpy Br-dapa,vdapa,dapb,dapb, dapep	-	-	MeCN, DMF	398 399
$PdCl_2L_2$, L: pyra, 3mpyra,4mpy	HCO_2^-	-0.77	MeCN	400
Pd, Co$(PPh_3)_2L$, L: 2m8OHqu2OHqx1OHiqu3OHiqudmbpy, 4mphen	CO CO, HCO_2^-	-1.01	MeCN MeCN+H_2O	401
Supported catalysis. Polymer films				
$[Ru^0(bpy)_2(CO)_2]_n$	CO	-0.91	H_2O	402 403 404 405 406 407 408
$[Ru^0(dmpy)_2(CO)_2]_n$	HCO_2^-	-0.46	H_2O	409
$[Ru(tpy)(CO)]_n$	HCO_2^-	-1.01	H_2O	410
$[Os^0(bpy)_2(CO)_2]_n$	CO HCO_2^-	-0.98	H_2O	411
Co$(tpy)_2$ incorporated in Nafion^{a}	HCO_2^-	-0.85 -1.06	H_2O	412
Fe, Ni,Co$(vtpy)_2$ electropolymerized	-	-	MeCN	413 414
Co$(vtpy)_2$ electropolymerized	HCO_2^-	-0.95	DMF	415
Cr,Fe, Ni,Co, Ru, Os$(vtpy)_2$ electropolymerized	HCHO	-0.85	H_2O	416
Metal-Sulfide Clusters				
Homogeneous catalysis				
$[Rh(C_5Me_5)]_3(\mu_3\text{-}S)_2$ $[Ir(C_5Me_5)]_3(\mu_3\text{-}S)_2$ $[Co(C_5H_4Me)]_3(\mu_3\text{-}S)_2$	$(CO_2)_2^{2-}$	-1.26 -1.01 -0.41	MeCN	417 418 419
Phosphine complexes (the ligands are shown in Scheme 36)				
Homogeneous catalysis				
RhL_2Cl, L: **1p**	HCO_2^-	-1.15	MeCN	420
PdLL', L: **2p**, L':CH_3CN,PPh_3, $P(OMe)_3$, PEt_3, $P(CH_2OH)_3$, Ni and Pt analogs are inactive	CO	-0.85	acidic MeCN	421
PdLsolvent, L: **3p, 4p**	CO	-0.85	acidic MeCN and DMF	422 423
PdLsolvent, L: **5p - 11p** O, S, N, As analogs are inactive	CO	-0.85	acidic MeCN and DMF	424 425 426
PdLsolvent, L: **12p, 13p**	CO	-0.85	acidic DMF buffered H_2O	427
PdLsolvent, L: **14p, 15p**	CO	-0.85	acidic DMF	428
$Pd_2L(solvent)_2$, L: **16p, 17p**	CO	-0.85	acidic DMF	429 430
Pd_nL, L: **18p, 19p**	CO	-0.85	acidic DMF	431
Ni_3 clusters **20p - 25p** Ni_2 clusters **26p - 28p**	CO HCO_2^-	-0.8	MeCN	432 433 434

a: electrolysis potential in V vs. SHE.

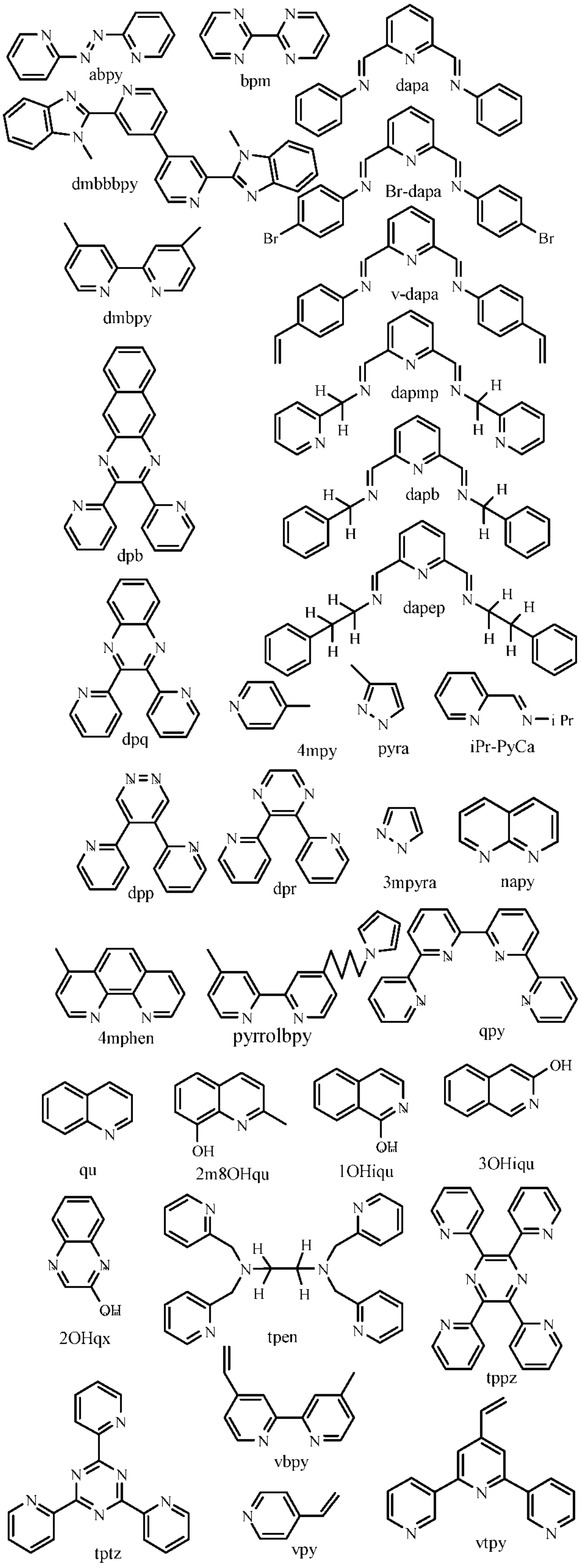
a: electrolysis potential in V vs. SHE.

kinetics may well be formally the same as in the redox catalytic mechanism. If this mechanism actually explains the exclusive formation of oxalate in this case, one consequence is that the double layer effect on CO_2 direct electrochemical reduction depicted in Scheme 30 may not be as important as previously thought.

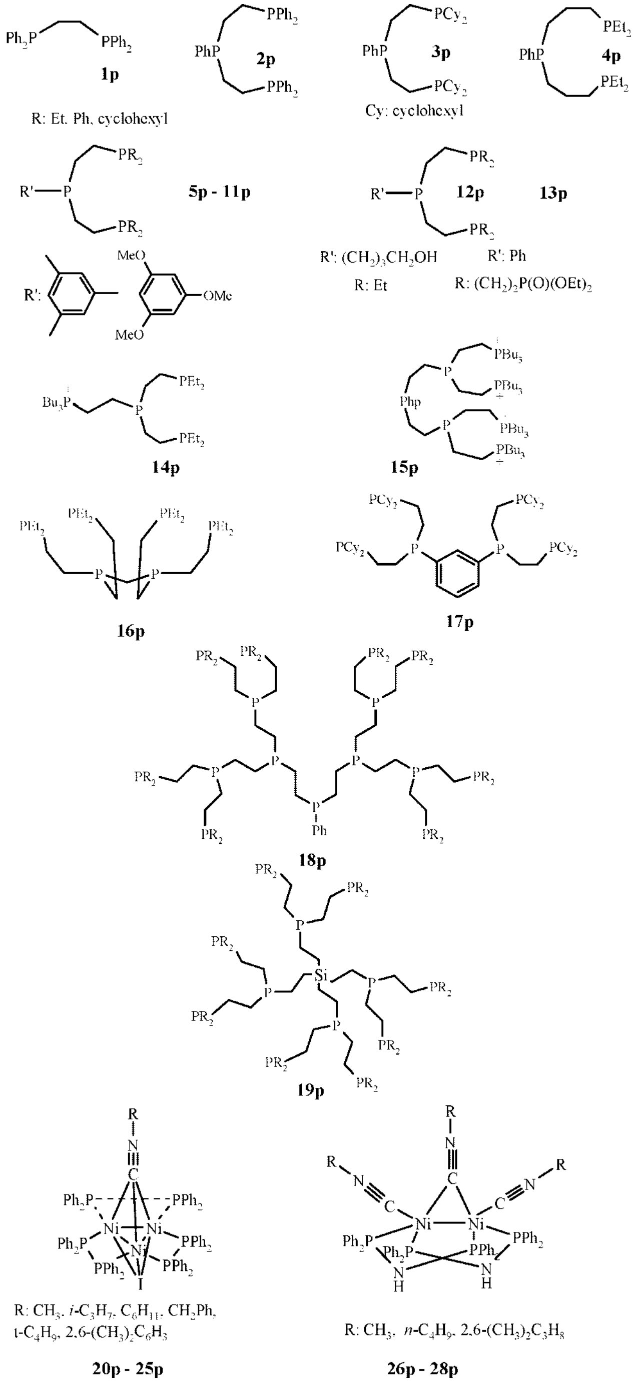
7.5. Chemical Catalysis: Families of Transition Metal Complex Catalysts

Chemical catalysis of CO_2 reduction is the realm of transition metal catalysts. Tables 2 and 3 summarize the observations made with the various families of complexes that have been used as chemical catalysts. They are catego-

Scheme 35. More Polypyridyl Ligands

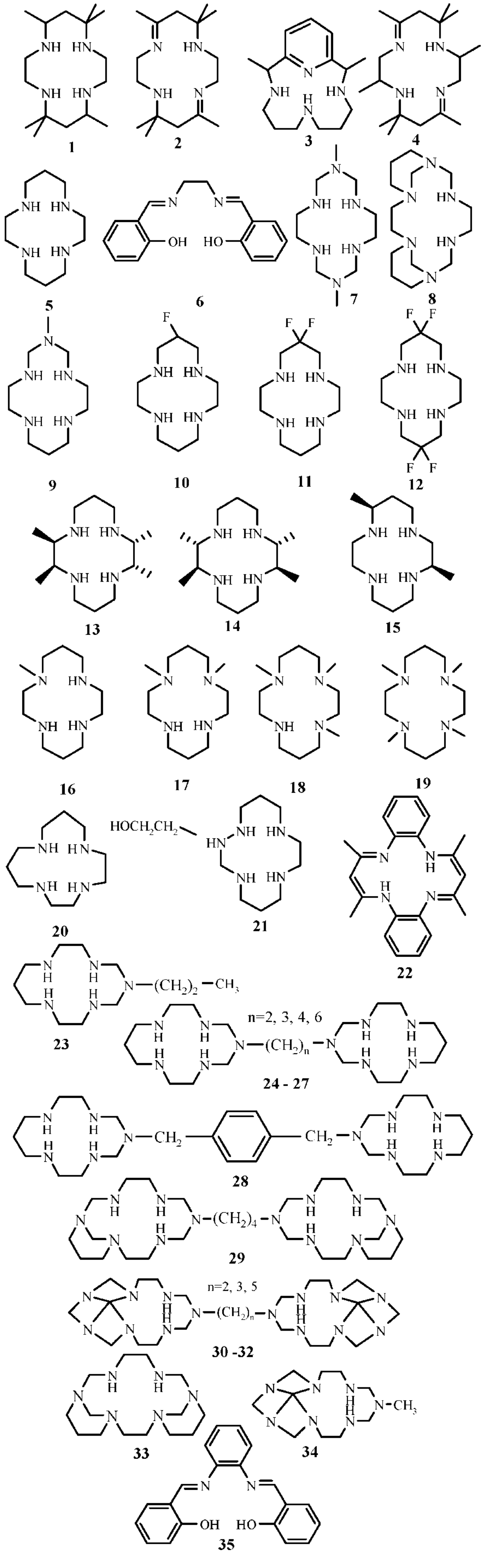


Scheme 36. Phosphine Ligands

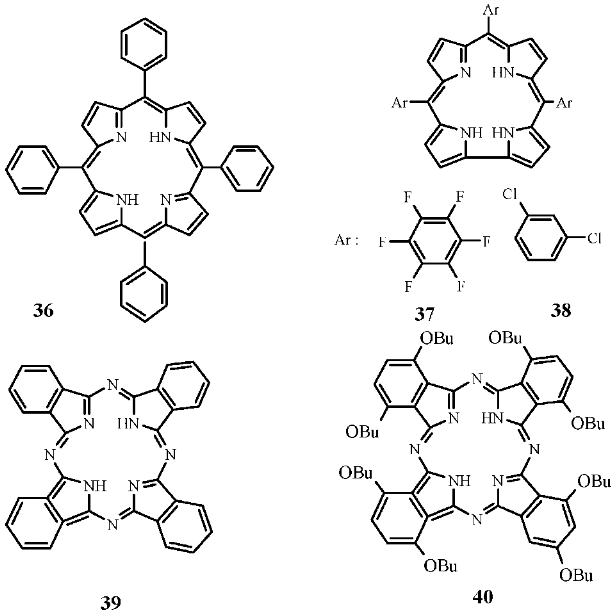


rized into four groups, polypyridyl rhenium complexes, other polypyridyl metal complexes, phosphine complexes, mostly of palladium (Table 2), cyclams and similar aza-macrocyclic complexes, porphyrins and similar macrocyclic complexes (Table 3). For each catalyst the table provides the definition of the complex with reference to appropriate schemes, the nature of the major products, the potential (referred to SHE) at which and the medium in which the preparative scale catalytic electrolysis has been carried out and the reference of the corresponding work. The values of these electrolysis potentials do not allow a rigorous comparison of the catalyst since the current densities are not necessarily the same in all cases. They nonetheless allow a quick estimate of their relative efficiency in terms of decrease of the overpotential. A number of catalytic systems have been tested in solution, but quite a few have also been immobilized on the electrode surface, according to various techniques, simple mixture with the electrode material, inclusion into a polymer, e.g. Nafion, electropolymerization of the ligand, which has been derivatized with a vinyl group beforehand. For each family of catalysts, Tables 2 and 3 have been accordingly divided in two successive sections corresponding to homogeneous and supported catalysis respectively.

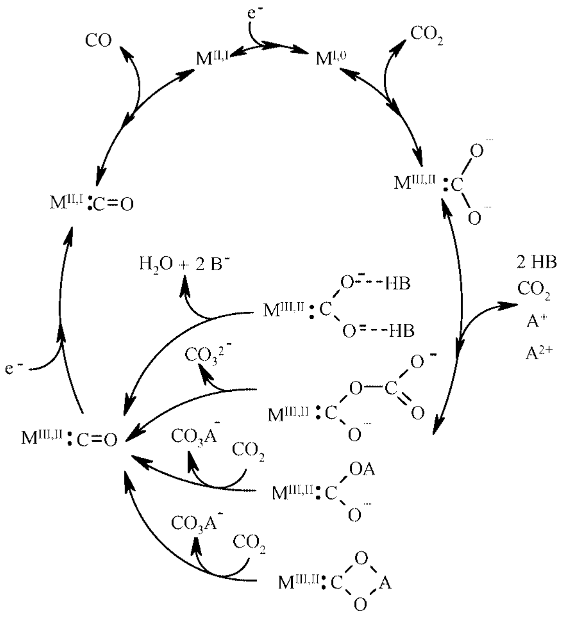
Scheme 37. Cyclams and Similar Aza-Macrocyclic Complexes



Scheme 38. Porphyrins and Similar Macrocyclic Complexes



Scheme 39

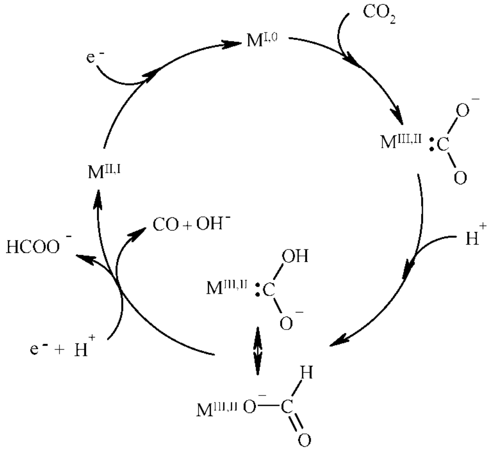


7.6. Chemical Catalysis. Mechanisms

Turning back to the discussion of oxalate formation addressed at the end of section 7.3, we note that Ir, Co and Rh trimetallic sulfide clusters offers a striking example of quantitative formation of oxalate with very low overpotentials[417–419] that do not match the redox catalysis mechanism. This observation points to the occurrence of a two-center mechanism similar to that depicted in Scheme 24.[468–470] The same is likely to be true with electropolymerized film of Re(vbpy)$(CO)_3$L.[360]

Among the huge number of catalysts that have been tested, the most common product is carbon monoxide, which is obtained at electrolysis potential values that clearly exclude a redox catalysis mechanism. There is therefore little doubt that the first step of the reaction sequence involves the formation of an adduct resulting from the inclusion of CO_2 in the coordination sphere of the metal, which has previously been reduced at the 1 or 0 oxidation state. Both oxidation

Scheme 40



Scheme 41

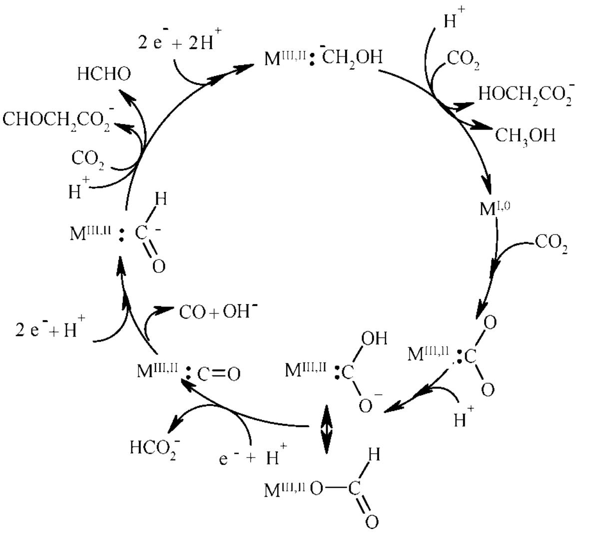


Table 3. Further Transition Metal Complex Catalysts of CO_2 Reduction

Complex	Products	E^a	Medium	Ref.
Cyclams and similar aza-macrocyclic complexes (the ligands are shown in Scheme 37.)				
Adsorbed on a mercury (and more rarely on a copper) electrode				
NiL, L: **1**, **2**, **3** CoL, L: **2**, **4**	CO	-1.05/-1.35	MeCN+H_2O H_2O	435
NiL, L: **5**	CO	-0.95/-1.05	H_2O	436 437 438
NiL, L: **1** CoL, L: **6**	CO	-1.15	MeCN+H_2O	439
NiL, L: **5**	-	-	H_2O	440 441 442
NiL, L: **7**, **8** (on Hg and Cu)	-	-	9-1 MeCN-H_2O	443
NiL, L: **9**	CO	-	H_2O	444
NiL, L: **5**, **10**, **11**, **12**	CO	-0.85	H_2O	445
NiL, L: **5**, **13**, **14**, **15**	CO	-0.75	H_2O	446
NiL, L: **5**, **16**, **17**, **18**, **19**	-	-	H_2O	447
NiL, L: **5**, **20**, **21**	-	-1.45	H_2O	448 449
mono and bis Ni complexes NiL, L: **5**, **23**, **33**, **34** Ni_2L, L: **24** - **32**	CO	-1.45	H_2O	450
CoL, L: **35**	CO	-1.35	MeCN	451
Supported catalysis. Polymer films				
NiL, L: **22** electropolymerized	HCO_2^-	-0.95	MeCN +2% MeOH	452
NiL, L: **5**, **16**, **17**, **18**, **19** incorporated in Nafion® or monolayer self-assembled	-	-	H_2O	453
Porphyrins and similar macrocyclic complexes (the ligands are shown in Scheme 38.)				
Fe(0)L, L: 36	CO	-1.55	DMF + weak Bronsted acids, e.g. CF_3CH_2OH or Lewis acids, e.g. Li^+, Mg^{2+}	454 455 456 457 458
Co L, L: 37 Fe L, L: 37, **38**	CO	-1.55	MeCN	459
Supported catalysis. Polymer films				
CoL, L: **36** attached to a glassy carbon electrode by a pyNHCO link	CO	-0.95	H_2O	460 461 462
CoL, L: **39, 40** in a poly(4-vinylpyridine) film	CO	-0.91	H_2O	463 464 465
ML, L: **39** M: Ti, V, Cr, Mo, Fe, Ru, Co, Ni, Pd, Cu, Zn, Cd, Ga, In, Ge, Sn and Pb. embedded in a carbon black and polytetrafluoroethylene Co and Ni are much more efficient than the other metals.	CO	-1.5/-1.75	H_2O	466 467

a: electrolysis potential in V vs. SHE.

states may be active as in the case of rhenium complexes.[353] One of the important parameters of the catalyst performance is the ability of creating such a reduced state able to bind CO_2 at the least negative potential possible. One expects a certain parallelism between negative potentials and high basicity of the reduced state thus created. The considerable number of empirical tries as to the nature of the metal and the ligand that have been successful in combining these apparently contradictory objectives clearly show that this rule is not strict. So far, no definite rules, even qualitative ones, emerge from perusing this abundant work. In this respect, the particular case of nickel cyclam is worth a particular mention: the complex is an excellent catalyst, but only when a mercury (and to a lesser extent a copper) electrode is used. Detailed studies[440–442] have shown that the active form of the catalyst is not plainly the nickel(I) cyclam but its adsorbed form on mercury, which possesses the ligation, geometry and electron density on Ni adequate for an efficient binding of CO_2.

The ligation characteristics and electron density on the metal are also essential parameters of the ensuing fate of the CO_2 adduct and of the nature of the products. The formation of CO requires the cleavage of one carbon−oxygen bond, which is not simply the result of an electron transfer to the primary adduct. Systematic reaction order studies are not numerous in the area. Among them the kinetic studies,[456–458] of the synergistic effect of the addition of weak Bronsted acids,[359,457] and of Lewis acids,[456,458] have suggested the mechanism depicted in Scheme 39 (in this scheme and in Schemes 40 and 41, after the first electron uptake, the further electron transfers may involve the electrode, and more likely for moderately fast follow-up steps, the initially reduced complex itself). These acids serve two purposes. One is to stabilize the primary CO_2 adduct. The second is to help the cleavage of the C−O bond leading to the formation of CO. In addition to weak Bronsted acids, including water, and to monovalent and divalent cation-Lewis acids, CO_2 itself may play the same double role. The same general reaction scheme is also consistent with the kinetic observations made with palladium−phosphine catalysts[421,422,424,427,429] including the role played by the second metal atom in dinuclear complexes.[429,430]

As in direct electrochemistry, formate is another two-electron product of the catalyzed reduction of CO_2. There is evidence that, at least in one case, formate may derive from the catalyst being a hydride donor to CO_2, leading to formate, rather than acting as an inner-sphere electron transfer.[376] However, this reaction pathway does not seem general. In most cases, the production of formate appears as the outcome of a competition in the $e^- + H^+$ transfer decomposition of the initial CO_2 adduct as sketched in Scheme 40.

In a few cases, higher reduction products have been obtained, including the formation of carbon−carbon bonds. This is the case with Ru(bpy)(tpy)(CO) in 8−2 EtOH−H_2O at −20 °C, where the product mixture contains CO, HCO_2^-, HCHO, CH_3OH, $H(O)CCO_2^-$ and $HOCH_2CO_2$.[379–383] The possibility of forming 4- and 6-electron products hinges upon the stabilization of the CO adduct toward expulsion of CO, obtained by decreasing the temperature. A route is then opened to further electron transfers coupled with proton and/or CO_2 transfers leading to the various products as depicted in Scheme 41.[471] Not only does temperature play an important role in the possibility of accessing 4- and 6-electron products, but the nature of the catalyst is also crucial: the above-mentioned products are not obtained with the closely related $Ru(bpy)_2(CO)_2$ complex under the same medium and temperature conditions. The stabilization of the CO adduct toward CO expulsion also allows the formation of acetone upon a two-electron reduction in the presence of a methylating agent, CH_3I, but also $(CH_3)_4N^+$, with other catalysts of the same family.[384–387]

7.7. Concluding Remarks

Although details are still lacking, the mechanisms of homogeneous redox and chemical catalysis of CO_2, leading to oxalate CO and formate, are reasonably well understood. The relationships between catalytic efficiency and structure remain essentially empirical. As with other catalytic reactions, the factors that govern the durability of the catalyst have been so far rarely analyzed. One may expect that the new energy and environment challenges will boost the need for a deeper comprehension of the catalytic routes of CO_2 reduction especially those leading to the formation of carbon−carbon bonds.

8. Conclusion

Since the first calculation of linear potential scan voltammograms for a one-step homogeneous catalysis of an electrochemical reaction,[6] theoretical tools have been made available that allow the kinetic characterization by nondestructive techniques, such as cyclic voltammetry, of catalytic mechanisms of any degree of complexity. As in other areas of electrochemical kinetics, realistic mechanism determination implies a correct appreciation of the number and nature of the independent parameters the system hinges upon and the examination of other mechanisms that would give rise to similar kinetic behaviors. Product distribution at preparative scale is also governed by similar parameters. The same remarks apply to catalysts immobilized in monolayer or multilayer films, where the transport of electrons and reactants through the coating may become rate-limiting factors of catalysis. The distinction between redox and chemical catalysis allows a first approach of predicting the catalytic efficiency. Indeed, redox catalysis involves outersphere electron donor or acceptor catalysts, and its rate is therefore limited by the activation−driving force relationships that characterize outersphere or dissociative electron transfers. Although redox catalysis is a useful tool for kinetic analysis of reactions involving short-lived intermediates, the above-mentioned limitations make chemical catalysis a preferred approach in terms of catalytic efficiency and in terms of specificity, including stereospecificity. From these points of view, the reductive dehalogenation of vicinal dibromides offers a striking example of the distinction between the two types of homogeneous catalysis, thanks not only to cyclic voltammetry but also to systematic preparative-scale investigations. Still dealing with carbon−halogen bond reductive cleavage, catalysis by vitamin B12 and reductive dehalogenases provides an example of how the redox vs chemical catalysis distinction can be applied fruitfully to mechanism analysis. These two examples also illustrate two types of chemical catalysis that have in common the existence of strong interactions between the active form of the catalyst and the substrate. One case is when the reaction of the active form of the catalyst is concerted with the regeneration of its starting form. There are a number of cases where the two processes are instead successive, meaning that a first intermediate has to be decomposed by electron transfer and, possibly, additional reactions to regenerate the catalyst. The reaction sequence then bears some resemblance with the "ping-pong" mechanism of enzymatic catalysis. Even if mechanism analysis is there more difficult and usually less conclusive, reduction of dioxygen, oxygen evolution from water oxidation and reduction of carbon dioxide provide additional examples of the superiority of chemical catalysis. In this domain, one is stricken by the ingenuity that has been developed to synthesize and test such a huge number of catalytic molecules. This may, at least partially, be a consequence of the fact that, unlike the case of redox catalysis, there no activation−driving force relationship that could serve as guidelines to the choice of the proper metal and the proper ligand. One of the most spectacular examples of this trial-and-error approach is probably the success, in terms of efficiency and durability, of CO_2 reduction catalysis by nickel cyclam under the condition that a mercury electrode is used, since, for still mysterious reasons, only an Hg-adsorbed form of the catalyst is active. A growing tendency of the current chemical catalytic studies is their biomimetic inspiration both in the search of efficient catalysts and in the purpose of a better understanding of the imitated natural system. This is true not only for dehalogenases as well as for oxygen reduction and evolution systems but also for hydrogen oxidation and production, not treated here. A note of regret regards the little attention paid to the durability of the catalysts so inventively conceived and synthesized. Attending data are indeed often absent as well as attempts to trace the mechanism by which catalyst deactivation occurs. There is little doubt that mechanistic issues will be more and more precisely addressed in the near future as contemporary energy and environment challenges will require intensification of research in the field.

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10. References

(1) The overpotential, or overvoltage, is the difference between the electrode potential and the equilibrium potential defined as $E_{eq} = E°$ $\pm [(RT)/F]\ln\{([A]^{a}_{eq}[B]^{b}_{eq}. .)/[C]^{c}_{eq}[D]^{d}_{eq}. .\}$, where $E°$ is the standard potential corresponding to the overall reaction and $[A]_{eq}$, $[B]_{eq}$, $[C]_{eq}$, $[D]_{eq}$ are the equilibrium activities of the reactants and products. The overpotential is thus different from the “driving force” of the reaction defined as the opposite of the standard free energy of the reaction: $\Delta G° = \pm F(E - E°)$, referred to the standard state of the reactant and product system.

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(5) Or any other two dimensionless parameters obtained from the combination of these two. Beyond the choice of the two parameters, the important point is that their number is two.

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