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Electrochemically Generated Transition Metal Complexes

Emissive and Reactive Excited States

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A variety of transition metal complexes (A) was subjected to an electrolysis by an alternating current in a simple undivided electrochemical cell. The compounds are reduced and oxidized at the same electrode. If the excitation energy of these compounds is smaller than the potential difference of the reduced (A^-) and oxidized (A^+) forms, back electron transfer may regenerate the complexes in an electronically excited state ($A^+ + A^- \rightarrow A^* + A$). These excited complexes may be emissive ($A^* \rightarrow A + h\nu$) and/or reactive ($A^* \rightarrow B$). Chemical transformations which accompany the ac electrolysis do not only proceed via excited states. As an important alternative the reduced or oxidized compounds can undergo a facile chemical change ($A^- \rightarrow B^-$ or $A^+ \rightarrow B^+$). Back electron transfer merely restores the original charges ($A^+ + B^- \rightarrow A + B$ or $A^- + B^+ \rightarrow A + B$). This mechanism and the ac electrolysis which proceeds via the generation of excited states are not unrelated processes. Hence the photoreaction and the ac electrolysis can lead to the same product irrespective of the intimate mechanism of the electrolysis. However, it is also possible that photolysis and electrolysis generate different products. Examples of ac electrolyses proceeding by these different mechanisms are discussed.

Bimolecular excited state electron transfer reactions have been investigated extensively during the last decade (1-3). Electron transfer is favored thermodynamically when the excitation energy E of an initially excited molecule A^* exceeds the potential difference of the redox couples involved in the electron transfer process.

$$A + h\nu \rightarrow A^*$$

$$A^* + B \rightarrow A^+ + B^- \qquad E(A^*) > E^o(A/A^+) - E(B^-/B)$$

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Studies of such systems provided a better understanding of the mechanism of electron transfer processes in general. This reaction type is also the basis of almost any type of natural or artificial photosynthesis. Hence it is not surprising that many investigations have been devoted to excited state electron transfer reactions. On the contrary, the reversal of excited state electron transfer has found much less attention although it is certainly not less interesting. In the present paper various aspects of this reaction type are discussed. The products of a redox reaction may be generated in an excited state if to a first approximation the excitation energy is smaller than the potential difference of the associated redox couples.

$$A^+ + B^- \rightarrow A^* + B \qquad E(A^*) < E^o(A/A^+) - E^o(B^-/B)$$

Generally, this energy requirement is only met when a strong oxidant reacts with a strong reductant. The excited state thus produced does not behave differently from that generated by light absorption. It can be deactivated by radiation or chemical transformations. Electron transfer induced emission (chemiluminescence, cl) is such a process. While it is well known for organic systems (4) there are not many observations of cl originating from transition metal complexes (5-12). The reactants can be prepared separately. Upon mixing, electron transfer takes place with concommitant emission of light. While this type of experiment is conceptionally very simple it may be difficult to accomplish due to practical or theoretical limitations. For example, this method cannot be applied when the redox partners A^+ and B^- are not very stable and have only a short lifetime. In this case the redox agents must be prepared in situ. This can be done in two different ways. The redox catalysis represents one possibility. It may apply to highly exoergic redox reactions which do not proceed rapidly due to large activation energies. A suitable redox catalyst may speed up this reaction and finally take up the energy which is released by this redox process.

Redox catalysis leading to cl is illustrated by two examples. The oxidation of oxalate by Pb(IV) does not proceed readily although it is strongly favored thermodynamically. This reaction is catalyzed by $Ru(bpy)_3{}^{2+}$ with bipy = 2,2'bipyridine according to the following mechanism (13):

$$2Ru(bipy)_3^{2+} + PbO_2 + 4H^+ \rightarrow 2Ru(bipy)_3^{3+} + Pb^{2+} + 2H_2O$$

$$Ru(bipy)_3^{3+} + C_2O_4^{2-} \rightarrow Ru(bipy)_3^{2+} + CO_2 + CO_2^-$$

$$Ru(bipy)_3^{3+} + CO_2^- \rightarrow [Ru(bipy)_3^{2+}]^* + CO_2$$

$$[Ru(bipy)_3^{2+}]^* \rightarrow Ru(bipy)_3^{2+} + h\nu$$

The reaction of $Ru(bipy)_3^{2+}$ with CO_2^- is the energy releasing electron transfer step leading to the formation of the electronically excited (*) complex. It cannot be carried out separately. The strong oxidant CO_2^- must be prepared in situ since it is a short-lived radical.

The catalyzed decomposition of energy-rich organic peroxides is another typical reaction of this type. It was called "chemically initiated electron-exchange luminescence" (CIEEL) by Schuster, who used organic compounds as redox catalysts (14). However, transition metal complexes work as well. The complex Re(o-phen)$(CO)_3$Cl (R) (o-phen = o-phenanthroline) catalyzes the decomposition of tetraline-hydroperoxide (T) to the ketone α-tetralone (K) and water according to the mechanism (15):

$$\begin{aligned} R + T &\rightarrow R^{+} + T^{-} \\ T^{-} &\rightarrow K^{-} + H_2O \\ R^{+} + K^{-} &\rightarrow R^{*} + K \\ R^{*} &\rightarrow R + h\nu \end{aligned}$$

The reaction of the ketyl radical anion with the oxidized rhenium complex is the energy-releasing electron transfer step. This reaction cannot be carried out separately. While ketyl radical anions are stable species, the oxidized complex is not stable and must be generated as short-lived intermediate.

Electrolysis represents another, very elegant method to prepare suitable redox pairs in situ which are generated by cathodic reduction and anodic oxidation. By application of an alternating current the redox pair is generated at the same electrode. Back electron transfer takes place from the electrogenerated reductant to the oxidant near the electrode surface. At an appropriate potential difference this annihilation reaction leads to the formation of excited products. As a result an emission (electrogenerated chemiluminescence, ecl) may be observed (16). Redox pairs of limited stability can be investigated by ac electrolysis. The frequency of the ac current must be adjusted to the lifetime of the more labile redox partner. Many organic compounds have been shown to undergo ecl (17-19). Much less is known about transition metal complexes. Most of the observations involve $Ru(bipy)_3^{2+}$ and related complexes which possess emissive charge transfer (CT) metal-to-ligand (M→L) excited states (13,20-31). The organometallic compound Re(o-phen)$(CO)_3$Cl is a further example of this category (32). Palladium and platinum porphyrins with emitting intraligand excited states are also ecl active (33). Under suitable conditions ecl was also observed for $Cr(bipy)_3^{3+}$ (27). In this case the emission originates from a ligand field (LF) excited state. Almost all of the ecl active transition metal complexes contain bipy or related ligands. It was therefore of interest to see if ecl could be extended to other types of transition metal compounds which have emitting states of different origin.

Furthermore, excited states generated electrochemically may be not only emissive but also reactive. The possibility of such an "electrophotochemistry" (epc) has been considered before (34). But real examples were discovered only quite recently and will be discussed later (35,36). However, chemical transformations induced by ac electrolysis may not only proceed via excited states. Other mechanisms can be also consistent with these observations. While this extends the range of reaction types of ac electrolysis, it complicates the elucidation of the real mechanism. Examples of the various reaction types are presented in the following sections.

Electrogenerated Chemiluminescence

For our ecl studies a very simple technique was employed. A 1-cm spectrophotometer cell was used as an undivided electrochemical cell. It was equipped with two platinum foil electrodes which were directly connected to a sine wave generator as an ac voltage source. Much more sophisticated methods have been described in the literature (16) but this simple design permitted the observation of ecl which appears at both electrodes.

Recently we observed ecl of the binuclear platinum complex tetrakis(diphosphonato)diplatinate(II) ($Pt_2(pop)_4^{4-}$) (37). This anion has attracted much attention due to its intense green luminescence in room temperature solution (38-40) (ϕ = 0.52) (41). The excited state of this complex undergoes oxidative (42) and reductive quenching (41). From the quenching experiments the redox potentials were estimated to be E^o = −1.4 V vs. SCE for the reduction and $E^o \sim 1$ V for the oxidation of $Pt_2(pop)_4^{4-}$ (41). The potential difference of 2.4 V almost matches the energy of the phosphorescing triplet (~ 2.5 eV) of $Pt_2(pop)_4^{4-}$. Consequently, it should be possible to observe ecl of this complex. However, the reduced ($Pt_2(pop)_4^{5-}$) (43) and oxidized ($Pt_2(pop)_4^{3-}$) (44,45) forms are not stable, but decay rapidly in solution. Hence an ecl of $Pt_2(pop)_4^{4-}$ will only take place if the subsequent generation of both redox partners occurs before they undergo a decay.

The ecl experiment was carried out in a solution of acetonitrile with Bu_4NBF_4 as supporting electrolyte (37). At an ac voltage of 4 V, a frequency of 280 Hz, and a current of 13 mA a green emission appeared at the electrodes. It was identical with the phosphorescence (λ_{max} = 517 nm) of $Pt_2(pop)_4^{4-}$. This observation is consistent with the following reaction sequence:

$$Pt_2(pop)_4^{4-} + e^- \rightarrow Pt_2(pop)_4^{5-} \qquad \text{cathodic cycle}$$

$$Pt_2(pop)_4^{4-} - e^- \rightarrow Pt_2(pop)_4^{3-} \qquad \text{anodic cycle}$$

$$Pt_2(pop)_4^{5-} + Pt_2(pop)_4^{3-} \rightarrow [Pt_2(pop)_4^{4-}]^* + Pt_2(pop)_4^{4-}$$

$$[Pt_2(pop)_4^{4-}]^* \rightarrow Pt_2(pop)_4^{4-} + h\nu$$

The reduction and oxidation of $Pt_2(pop)_4^{4-}$ takes place at the same electrode. Back electron transfer generates one of the starting ions in the excited triplet state which undergoes phosphorescence. Interestingly, the fluorescence of the complex which appears on photoexcitation at λ_{max} = 407 nm, is not observed in the ecl experiment. This is not surprising since the back electron transfer does not provide enough energy (~ 2.4 V) to populate the emitting singlet (~ 3.3 V).

It should be mentioned here that the processes which are involved in the appearance of an ecl of $Pt_2(pop)_4^{4-}$ are associated with changes in the metal-metal bonding of this binuclear complex (38-40, 42,44,46,47). The Pt-Pt bond order which is zero in the ground state is increased to 0.5 by oxidation as well as by reduction. The annihilation reaction leads to the formation of $Pt_2(pop)_4^{4-}$ as the ground (bond order = 0) and excited state (bond order = 1). A related case which was reported quite recently is the ecl of $Mo_6Cl_{12}^{2-}$. The metal-

metal bonding of the cluster is involved in the redox processes which are associated with the ecl (48).

Electrogeneration of Excited Complexes Undergoing Emission and Reaction

The electrochemical generation of excited states may not only lead to an emission. In addition or as an alternative the excited state can undergo a chemical reaction ("electrophotochemistry", epc) as it would occur upon light absorption (photochemistry). In the ecl experiments the observation of luminescence is by itself a proof for the generation of excited states. But the fact that electrolysis and photolysis both lead to the formation of the same product does not prove the electrochemical generation of an excited state (see below). For this reason it is an advantage to study compounds which are simultaneously photoemissive and photoreactive. A positive correlation between ecl and the electrochemical reaction is a good indication that the chemical transformation is indeed associated with an excited state. In this case the electrochemical reaction is a true epc. Upon ac electrolysis the complex $Ru(bipy)_3^{2+}$ undergoes simultaneously ecl and epc (49).

The well-known photoluminescence of $Ru(bipy)_3^{2+}$ occurs from the lowest excited state which is of the CT (Ru→bipy) type (50,51). The emission appears in aqueous as well as in non-aqueous solutions. While the complex is hardly light-sensitive in water (52) it can undergo an efficient photosubstitution of a bipy ligand in non-aqueous solvents (50,51,53-56). The reactive excited state seems to be a LF state which lies at slightly higher energies but can be populated thermally from the emitting CT state (50-52,55-58). According to these observations the electrochemical generation of excited $Ru(bipy)_3^{2+}$ in non-aqueous solutions should not only be accompanied by the well-known ecl but also by an epc. Moreover, the efficiency of both processes should show a positive correlation. Preliminary experiments indeed provide evidence for a simultaneous occurance of ecl and epc of $Ru(bipy)_3^{2+}$ (49).

An ac electrolysis of $[Ru(bipy)_3]Cl_2$ was carried out in a spectrophotometer cell as an undivided electrochemical cell equipped with platinum foil electrodes. Acetonitrile was used as solvent and Bu_4NBF_4 served as supporting electrolyte. The electrolysis led to the typical ecl of $Ru(bipy)_3^{2+}$ (20,21,23,25). Simultaneously, the complex underwent a chemical change. The spectral variations which accompanied the electrolysis (Figure 1) were very similar to those observed during the photolysis of the same solution (λ_{irr} > 335 nm). The product of electrolysis and photolysis was not yet identified definitely, but according to a preliminary characterization it seems to be $[Ru(bipy)_2(CH_3CN)Cl]^+$. However, it is important to note that all changes of the experimental conditions (e.g. variations of the ac frequency, stirring of the solution) which lead to a change of the ecl intensity also caused a corresponding change of the efficiency of the electrochemical reaction. These observations are good indication that both processes proceed via the generation of excited $Ru(bipy)_3^{2+}$. It is suggested that the ac electrolysis can be described by the following mechanism:

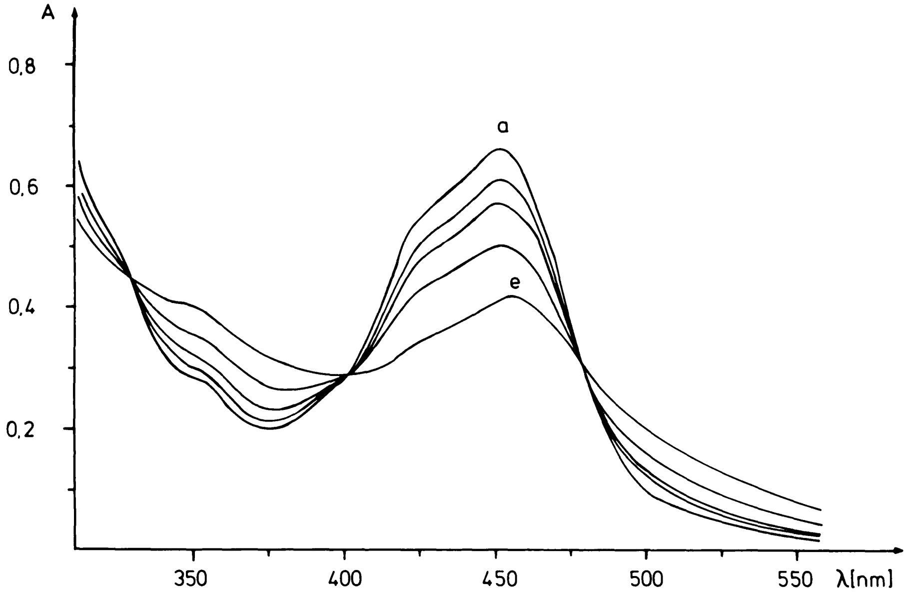

Figure 1. Spectral changes during ac electrolysis of 10^{-4} M $[Ru(bipy)_3]Cl_2$ in acetonitrile/0.1 M Bu_4NBF_4 at (a) 0 and (e) 120 - min electrolysis time at 3 V/20 Hz and 30 mA, 1-cm cell.

$$\begin{aligned}
&\mathrm{Ru(bipy)_3^{2+} + e^-} &&\rightarrow \mathrm{Ru(bipy)_3^{+}} &&\text{cathodic cycle}\\
&\mathrm{Ru(bipy)_3^{2+} - e^-} &&\rightarrow \mathrm{Ru(bipy)_3^{3+}} &&\text{anodic cycle}\\
&\mathrm{Ru(bipy)_3^{+} + Ru(bipy)_3^{3+}} &&\rightarrow \mathrm{[Ru(bipy)_3^{2+}]^*} &&\\
& &&\quad \mathrm{+Ru(bipy)_3^{2+}} &&\text{annihilation}\\
&\mathrm{[Ru(bipy)_3^{2+}]^*} &&\rightarrow \mathrm{Ru(bipy)_3^{3+}} + h\nu &&\text{ecl}\\
&\mathrm{[Ru(bipy)_3^{2+}]^* + Cl^- + CH_3CN} && &&\\
& &&\rightarrow \mathrm{Ru(bipy)_2(CH_3CN)Cl^+} &&\\
& &&\quad \mathrm{+\ bipy} &&\text{epc}
\end{aligned}$$

The conclusion that the electrochemical reaction of $\mathrm{Ru(bipy)_3^{2+}}$ takes place via an excited state is also supported by other observations. According to electrochemical studies the reduced and oxidized complexes $\mathrm{Ru(bipy)_3^{+}}$ and $\mathrm{Ru(bipy)_3^{3+}}$ are fairly stable and not expected to undergo rapid chemical transformations (21,23,25,50).

Electrogeneration of Reactive Excited States

Most compounds which undergo a photochemical reaction do not simultaneously show photoluminescence. It is then more difficult to prove that a reaction induced by ac electrolysis proceeds via the intermediate formation of excited states. A different mechanism may be in operation. In this case the chemical transformation occurs in the reduced and/or oxidized form. The back electron transfer merely regenerates the charges of the starting compound:

$$\begin{aligned}
&A + e^- &&\rightarrow A^- &&\text{cathodic cycle}\\
&A - e^- &&\rightarrow A^+ &&\text{anodic cycle}\\
&A^- &&\rightarrow B^- &&\text{chemical reaction}\\
&A^+ + B^- &&\rightarrow A + B &&\text{annihilation}
\end{aligned}$$

Nevertheless, the result of the electrolysis may be the same as that of the photolysis, because the origin of the reactivity is similar in both cases. For example, a bond weakening may occur upon reduction or oxidation since an electron is added to an antibonding π^* orbital or removed from a bonding π orbital. The same changes take place upon $\pi\pi^*$ excitation.

A case in question is the ac electrolysis of the complex $\mathrm{Re(trans\text{-}SP)_2(CO)_3Cl}$ (SP = 4-styrylpyridine) (59). It was shown before that the coordinated ligand SP undergoes a photochemical trans/cis isomerization (60). The reactive excited state is the lowest $\pi\pi^*$ intraligand (IL) state, which is not luminescent. The ac electrolysis leads also to the trans/cis isomerization of the coordinated ligand (59). Hence it is a reasonable assumption that the electrolysis proceeds via the generation of the $\pi\pi^*$ IL state:

$$\mathrm{Re(trans\text{-}SP)_2(CO)_3Cl} + e^- \rightarrow \mathrm{Re(trans\text{-}SP)_2(CO)_3Cl^-}$$

$$\mathrm{Re(trans\text{-}SP)_2(CO)_3Cl} - e^- \rightarrow \mathrm{Re(trans\text{-}SP)_2(CO)_3Cl^+}$$

$$\mathrm{Re(trans\text{-}SP)_2(CO)_3Cl^+} + \mathrm{Re(trans\text{-}SP)_2(CO)_3Cl^-}$$

$$\rightarrow \mathrm{Re(trans\text{-}SP)_2(CO)_3Cl^*} + \mathrm{Re(trans\text{-}SP)_2(CO)_3Cl}$$

$$\mathrm{Re(trans\text{-}SP)_2(CO)_3Cl^*} \rightarrow \mathrm{Re(cis\text{-}SP)_2(CO)_3Cl}$$

However, as an alternative the isomerization may take place in the reduced and/or oxidized form:

$$\mathrm{Re(trans\text{-}SP)_2(CO)_3Cl^-} \rightarrow \mathrm{Re(cis\text{-}SP)_2(CO)_3Cl^-}$$

$$\mathrm{Re(trans\text{-}SP)_2(CO)_3Cl^+} \rightarrow \mathrm{Re(cis\text{-}SP)_2(CO)_3Cl^+}$$

$$\mathrm{Re(cis\text{-}SP)_2(CO)_3Cl^+} + \mathrm{Re(cis\text{-}SP)_2(CO)_3Cl^-}$$

$$\rightarrow 2\ \mathrm{Re(cis\text{-}SP)_2(CO)_3Cl}$$

Inspection of some additional data does not lead to a distinction between the two possibilities. The potential difference of the reduced and oxidized complex (2.94 V) exceeds the electronic excitation energy of the neutral complex (~ 2.1 eV) (59). On energetic grounds the electrochemical generation of excited states is certainly possible. The related complex Re(o-phen)(CO)$_3$Cl is not light sensitive but is photoluminescent and also ecl active (32). By analogy one might assume that the electrolysis of both complexes proceeds by the same mechanism. On the other side, cyclic voltammetry shows that the oxidized form of Re(trans-SP)$_2$(CO)$_3$Cl is fairly stable but the reduced complex decays irreversibly (59). Only at large scan rates (100 Vs^{-1}) the reduction wave shows beginning reversibility. It is then not unreasonable to assume that the ligand isomerization takes place in the reduced complex. The final back electron transfer would merely restore the neutral complex. Of course, in the absence of ecl any direct proof of the electrochemical generation of excited states is difficult to obtain. Nevertheless, indirect but conclusive evidence showed indeed that an excited state mechanism led to the electrochemical isomerization of the complex.

Experiments were carried out to determine if during the ac electrolysis the ligand isomerization requires the formation of the reduced and oxidized form (59). This would indicate an excited state mechanism. If the intermediate formation of the reduced or oxidized complex is sufficient to induce the isomerization, excited states are not required. First support in favor of a true epc was obtained by the results of the ac electrolysis of Re(trans-SP)$_2$(CO)$_3$Cl in the presence of redox buffers. Tetramethyl-p-phenylenediamine (TMPD) was used as reductant and the paraquat cation (PQ^{2+}) served as oxidant. In the presence of an excess of TMPD the complex is still reduced, but TMPD is oxidized during the electrolysis. Since the oxidation potential of TMPD is much lower than that of the complex, the annihilation reaction of the complex anion and TMPD$^+$ does not provide enough energy to generate the complex in the excited state. Quite an analogous situation applies to the electrolysis in the presence of PQ^{2+}. Now the complex is oxidized but PQ^{2+} reduced. Again, the potential difference of the complex cation and PQ^{+} is smaller than the excitation energy of Re(trans-SP)$_2$(CO)$_3$Cl. In both experiments the ligand isomerization was essentially suppressed. Consequently the intermediate formation of the complex cation or anion alone cannot be responsible for the isomerization.

Additional evidence in support of an excited state mechanism was obtained by continuous potential step chronocoulometric experiments (59). When the electrode potential was stepped only over the oxidation potential of the complex at a frequency of 10 Hz a slow net oxidation took place. Potential steps involving only the reduction wave led to rapid net reduction but no ligand isomerization. The isomerization occurred only when the potential steps included both reduction and oxidation of the complex. Since the voltammograms of Re(trans-SP)$_2$(CO)$_3$Cl and Re(cis-SP)$_2$(CO)$_3$Cl are virtually indistinguishable, the ligand isomerization was not accompanied by a potential change. No net Faradaic process was observed.

The conclusion that the ac electrolysis of Re(trans-SP)$_2$(CO)$_3$Cl proceeds via excited states is also supported by the direction of isomerization. In thermal reactions of stilbene derivatives and radicals cis to trans conversions are generally observed (61). Contrary to this behavior the photolysis and ac electrolysis lead to energetically uphill trans to cis isomerization.

AC Electrolysis Without Generation of Excited States

As discussed above, a chemical transformation which occurs during the ac electrolysis does not require the intermediate formation of excited states. The chemical reaction may take place in the reduced and/or oxidized form of a compound. Nevertheless, in this case the electrolysis may still lead to the same products as those of the photolysis due to the obvious relationship between electronic excitation and redox processes. It will be then quite difficult to elucidate the mechanism of electrolysis. This reaction type may apply to the electrochemical substitution of $Cr(CO)_6$ (59).

The ac electrolysis of $Cr(CO)_6$ in CH_3CN was accompanied by the same spectral changes (Figure 2) as those observed in the photolysis of the same solution with 333-nm light. In both cases $Cr(CO)_6$ was converted to $Cr(CO)_5(CH_3CN)$ (59). According to Pickett and Pletcher (62) $Cr(CO)_6$ shows a reversible oxidation wave at 1.52 V vs. SCE; the reduction wave at -2.66 V is irreversible and was attributed to a rapid or even concerted loss of CO from $Cr(CO)_6^-$ to give $Cr(CO)_5^-$. A reverse peak in the cyclic voltammogram at -2.1 V shows the reoxidation of the latter species to the coordinatively unsaturated $Cr(CO)_5$ which can be stabilized by the addition of a solvent molecule as a sixth ligand. Consequently, the ac electrolysis may proceed according to the following reaction scheme without invoking an electronically excited state in the back electron transfer (59):

$Cr(CO)_6 - e^- \rightarrow Cr(CO)_6^+$ anodic cycle

$Cr(CO)_6 + e^- \rightarrow Cr(CO)_6^-$ cathodic cycle

$Cr(CO)_6^- \rightarrow Cr(CO)_5^- + CO$ ligand dissociation

$Cr(CO)_6^+ + Cr(CO)_5^- \rightarrow Cr(CO)_6 + Cr(CO)_5$ annihilation

$Cr(CO)_5 + CH_3CN \rightarrow Cr(CO)_5(CH_3CN)$ ligand addition

This mechanism and the photolysis have in common that the addition of an electron to the antibonding e_g orbitals induces the dissociation of a CO ligand.

As a further possibility the ac electrolysis may lead to other products than those of the photolysis. In this case an excited state mechanism is, of course, excluded. Although there is a certain similarity between the electronic structure of an excited state and the reduced or oxidized form of a molecule, they are not identical. Consequently, it is not surprising when photolysis and electrolysis do not yield the same product. Another reason for such an observation may be the different lifetimes. An excited state can be extremely short-lived. Non-reactive deactivation could then compete successfully with a photoreaction. The compound is not light-sensitive. On the contrary, the reduced and oxidized intermediates generated by ac electrolysis should have comparably long life times which may permit a reaction. The ac electrolysis of Ni(II)(BABA)(MNT) (BABA = biacetylbis(anil) and MNT^{2-} = disulfidomaleonitrile) is an example of this reaction type (63).

The complex Ni(BABA)(MNT) (64) is not light sensitive ($\lambda_{irr} >$ 400 nm) in solutions of acetonitrile but undergoes an ac electrolysis which is accompanied by spectral changes as shown in Figure 3. According to a preliminary analysis of the products the electrolysis leads to a ligand exchange:

$$2\ Ni^{II}(BABA)(MNT) \rightarrow Ni^{II}(BABA)_2^{2+} + Ni^{II}(MNT)_2^{2-}$$

The electrochemistry of Ni(BABA)(MNT) has been investigated recently (64). The first reduction occurs reversibly at $E_o' = -0.7$ V vs. SCE. However, the oxidation is irreversible ($E_{P/2} = 0.8$ V). For the related complex $Ni(o\text{-}phen)(S_2C_2Ph_2)$ it was shown that the cation $Ni(o\text{-}phen)(S_2C_2Ph_2)^+$ generated by photooxidation in halocarbon solvents undergoes a facile ligand exchange to yield the symmetric complexes $Ni(o\text{-}phen)_2^{2+}$ and $Ni(S_2C_2Ph_2)_2$ (65). According to these considerations the ac electrolysis can be rationalized by the following reaction scheme:

$Ni(BABA)(MNT) + e^- \rightarrow Ni(BABA)(MNT)^-$ cathodic cycle

$Ni(BABA)(MNT) - e^- \rightarrow Ni(BABA)(MNT)^+$ anodic cycle

$2\ Ni(BABA)(MNT)^+ \rightarrow Ni(BABA)_2^{2+} + Ni(MNT)_2$ ligand exchange

$2\ Ni(BABA)(MNT)^- + Ni(MNT)_2 \rightarrow 2\ Ni(BABA)(MNT) + Ni(MNT)_2^{2-}$ electron transfer

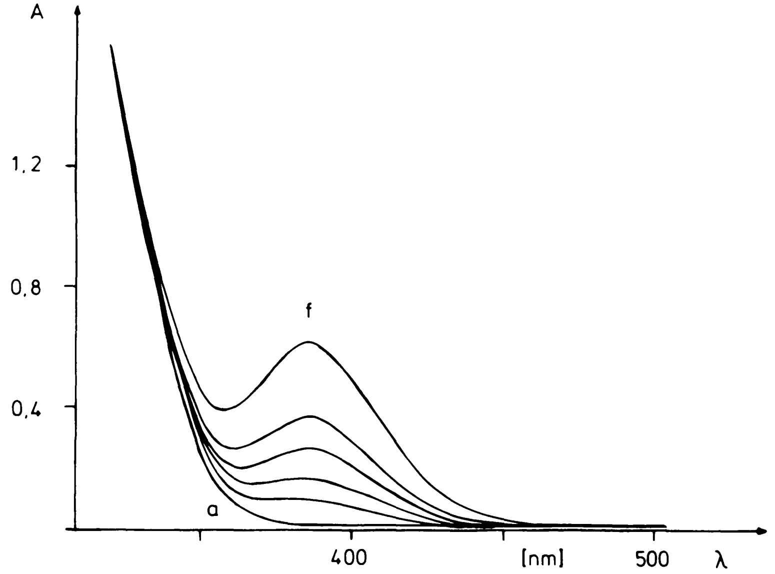

Figure 2. Spectral changes during ac electrolysis of 6.5×10^{-4} M $Cr(CO)_6$ in acetonitrile/0.05 m Bu_4NBF_4 at (a) 0 and (f) 300-min electrolysis time at 2.5 V/10 Hz and 5 mA, 1-cm cell.

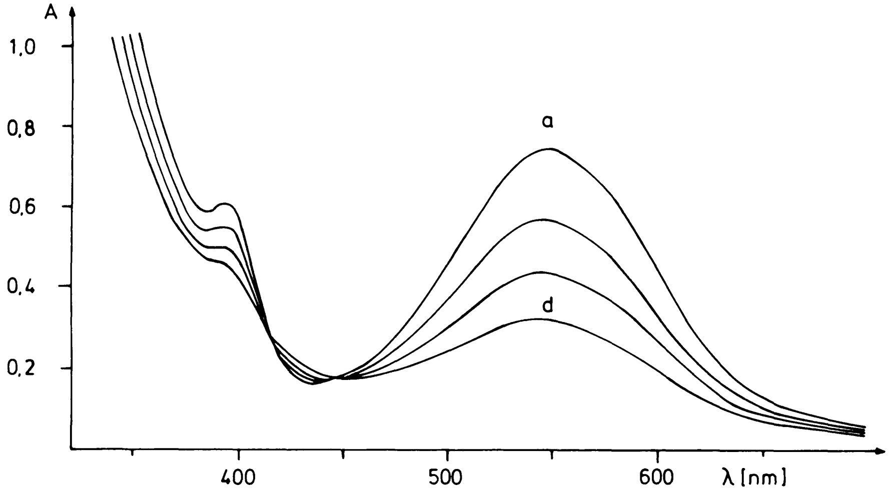

Figure 3. Spectral changes during ac electrolysis of 1.5×10^{-4} M Ni(BABA)(MNT) in acetonitrile/0.1 M Bu_4NBF_4 at (a) 0 and (d) 30-min electrolysis time at 3 V/20 Hz and 40 mA, 1-cm cell.

The ligand exchange produces $Ni(MNT)_2$ which is not stable but a strong oxidant (66). It oxidizes apparently the reducing anion $Ni(BABA)(MNT)^-$ in two subsequent electron transfer steps.

Reactions Related to the AC Electrolysis

There are other reactions of transition metal complexes which are relevant to our observations on the ac electrolysis. Recently, new mechanisms of ligand substitution reactions have been reported which are characterized by electron transfer reactions as key steps although the overall reactions are not redox processes, e.g.,

$$
\begin{array}{lll}
 & ML + e^- \rightarrow ML^- & \\
 & ML^- + L' \rightarrow ML'^- + L & \\
 & ML'^- - e^- \rightarrow ML' & \\
\hline
\text{overall:} & ML + L' \rightarrow ML' + L &
\end{array}
$$

The substitutionally labile complex may be generated not only by reduction but by oxidation as well. An immediate relationship of such a reaction to the ac electrolysis proceeding without generation of excited states can be recognized. The initial production of the substitutionally labile oxidation state of ML can be achieved electrochemically (67-76), chemically (75-77) or photochemically (78). In the electrochemical experiments reduction or oxidation was accomplished by a direct current. In most cases these processes are catalytic chain reactions with Faradaic efficiencies much larger than unity. Electrochemical substitution of $M(CO)_6$ with M = Cr, Mo, W was carried out by cathodic reduction to $M(CO)_6^-$ which dissociates immediately to yield $M(CO)_5^-$. Upon anodic reoxidation at the other electrode coordinatively unsaturated $M(CO)_5$ is formed and stabilized by addition of a ligand L to give $M(CO)_5L$ (68).

Photochemical substitution via a labile oxidation state may occur by excited-state electron transfer. If the metal complex has a long-lived excited state, it can undergo an electron exchange with a reductant or oxididant in a bimolecular reaction. The labile reduced or oxidized complex thus produced is susceptible to a ligand substitution. A catalytic chain reaction takes place when the substituted complex in the labile oxidation state undergoes a further electron exchange with another unsubstituted complex. The chain terminates by back electron transfer between the labile oxidation state and the external redox partner which was generated initially. The cation $Re(o\text{-}phen)(CO)_3(CH_3CN)^+$ undergoes this new type of photosubstitution (78). The occurrence of a chain reaction was confirmed by the quantum yields which were as large as $\phi = 24$ depending on the experimental conditions. Of course, the efficiency of the usual photosubstitutions which originate from LF excited states of metal complexes do not exceed unity.

Conclusion

The use of ac electrolysis in all its variations is certainly an interesting and valuable technique for study of the mechanism of electron transfer reactions. The generation of a short-lived redox pair as chemical intermediates is an important feature of the ac electrolysis. In the future it may even be developed to synthetic applications irrespective of the mechanistic details. In some cases it could be a convenient alternative to photochemical reactions. In other cases it represents a new reaction type which has no precedent.

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