Activation of Complexes by Electron-Transfer Processes

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Abstract

The electrochemical behaviours of *cis*-[ReCl(NCC_6H_4Me-4)$(dppe)_2$] and of the hydride complex [ReClH(NCC_6H_4Cl-4)$(dppe)_2]^+$ have been studied by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) in aprotic media and at platinum electrodes. The 16-electron dicationic configuration of the former compound undergoes a facile isomerization to its *trans* isomer in the time scale of CV whereas the hydride complex undergoes an anodically induced deprotonation through an overall bimolecular process. Quantitative analyses of both processes, by digital simulation of cyclic voltammograms, are outlined.

The models of *Amavadine* $[VL_2]^{2-}$ [L = $^-ON(CH(CH_3)COO^-)_2$ ($HIDPA^{3-}$) or $^-ON(CH_2COO^-)_2$ ($HIDA^{3-}$)], act as electron-transfer mediators in the electrocatalytic oxidation of thiols. This redox catalysis process is shown to occur through an unprecedented mechanism involving Michaelis-Menten type kinetics.

Introduction

Cyclic voltammetry is a common dynamic method in electroanalytical chemistry which has been applied increasingly to the study of several phenomena in metal complexes, providing direct kinetic information of electrode reactions which include both heterogeneous and homogeneous electron-transfer steps as well as coupled chemical reactions.

The use of modern numerical methods, in particular digital simulation of cyclic voltammetry, facilitate calculation of voltammetric curves for complex systems therefore enabling the global estimate of both thermodynamic and kinetic parameters

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Some results will be outlined on the application of Molecular Electrochemistry to the study of charge transfer induced isomerizations, metal-hydrogen bond cleavages and electrocatalytic processes involving transition-metal complexes.

Electrochemically induced *cis*-to-*trans* isomerization

of the nitrile complexes [ReCl(NCR)(dppe)$_2$]

The *cis*-[ReCl(NCR)(dppe)$_2$] complexes constitute rare examples of *cis* isomers of octahedral rhenium(I) tetraphosphine compounds containing a π-acceptor (NCR) and a π-donor (Cl) ligand bonded to the Re(dppe)$_2^+$ core, a combination of ligands which has not been previously studied through extended Hückel MO calculations. In this system geometrical isomerization induced by two-electron charge transfer is observed at the level of the 16-electron complex and a detailed mechanistic study of the isomerization process was accomplished in the particular case of R = NCC_6H_4Me-4 [1].

The *cis* and *trans* isomer of [ReCl(NCC_6H_4Me-4)(dppe)$_2$] were synthesised according to published procedures [2,3] and their electrochemical behaviour investigated by CV and CPE. They exhibit two successive one-electron anodic waves (Table 1). While the second wave occurs at analogous potentials for both isomers, the first one exhibits an oxidation potential which clearly depends on the isomer with the *trans* one being oxidised at a considerable lower potential than the corresponding *cis* compound.

Table 1: Cyclic voltammetric data[a] for *cis*- and *trans*-[ReCl(NCC_6H_4Me-4)(dppe)$_2$].

	trans- isomer	*cis*- isomer
$^{I}E^{o}$	-0.31	-0.13
$^{II}E^{o}$	0.67	0.70

[a] Potentials in V *vs.* SCE, measured at a Pt disc electrode (ϕ = 500 μm); scan rate of 200 mV s^{-1}; 0.2 mol dm^{-3} [NBu_4][BF_4] - thf. CV for the *cis*-isomer was performed at 273K.

CPE on the plateau of the first wave of the neutral *trans* isomer (Fig. 1) consumes 1 faraday/mol to afford the stable monocationic *trans* complex. Similarly, and despite

the chemically reversible character of wave II, CPE at this level consumes 2 faraday/mol with degradation of the resulting species.

Although at high scan rates the cyclic voltammetry of the neutral *cis* isomer is very reminiscent of that of the *trans* isomer showing apparently two successive one-electron chemically reversible anodic waves, some important features are relevant.

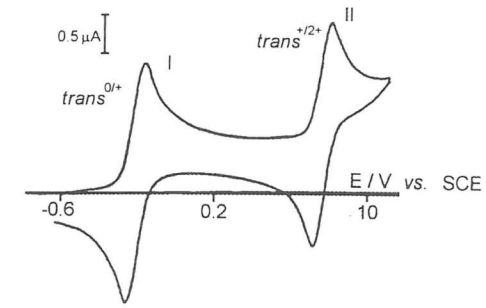


Fig. 1 - Cyclic voltammogram for *trans*-[ReCl(NCC_6H_4Me-4)(dppe)$_2$] (3.6 mM) in thf with 0.2 M [NBu_4][BF_4]. ν = 200 mV s^{-1}.

Indeed, at low scan rates the first wave remains fully reversible only if the potential scan is reversed between the two waves, since if it is reversed after the second wave the reduction part of it becomes broad, ill-defined, due to the overlapping of the *cis*$^{2+}$ and *trans*$^{2+}$ species, therefore featuring an incomplete isomerization because of the short time scale used (Fig. 2). In agreement, at even lower scan rates this wave becomes sharp since only the reduction part of the dicationic *trans* species is observed which clearly indicates a complete *cis*$^{2+}$ to *trans*$^{2+}$ isomerization at this time scale.

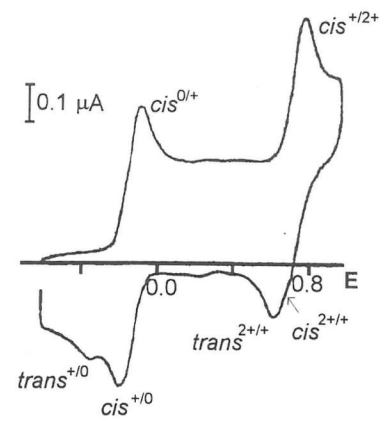
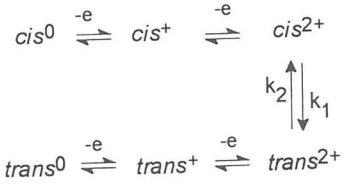


Fig. 2 - Cyclic voltammogram of *cis*-[ReCl(NCC_6H_4Me-4)(dppe)$_2$] (0.6 mM) in thf with 0.2 M [NBu_4][BF_4]. ν = 800 mV s^{-1}.

Therefore, a quantitative evaluation of the kinetics of the isomerization is impossible on the basis of the second waves due to the overlapping of the reduction waves of the two dications. This becomes easier at the level of the reduction of the *cis* and *trans* monocations since their waves are well apart. Here it was possible to check that the isomerization takes place without involvement of any other chemical process in the time scale of cyclic voltammetry, since at any scan rate, and for any concentration, the sum of the peak currents of both reduction waves is

equal to the peak current of the cis^0 oxidation wave.

However, when the scan rate is decreased the size of the cis^+ reduction wave increases at the expense of the $trans^+$ wave, a behaviour which cannot be accounted for by considering the effect of diffusion [3] and which indicates that a chemical reaction converting the *trans* isomer back to the *cis* isomer must be considered. The only sequence that is compatible with all the experimental data [3] is the one described in scheme 1.



Scheme 1

The working curves depicted in figure 3 take into account all the necessarily involved [3] homogeneous electron transfers and represent the predicted variations of the yield in $trans^+$ species, given by the factor $\rho = i_p(trans^{+/0})/i_p(cis^{0/+}) = i_p(trans^{+/0})/i_p(trans^{+/0} + cis^{0/+})$ as a function of the dimensionless parameter $k_1(RT/F\nu)$ for the cis^{2+} to $trans^{2+}$ isomerization step considered in scheme 1, giving the set of values $k_1 = 5.6 \pm 0.3\ s^{-1}$ and $k_2 = 1.0 \pm 0.1\ s^{-1}$. They were determined using a simulation programme based on explicit finite difference procedures, developed by Dr. Christian Amatore by using Turbo-Pascal 5.0 programming [3].

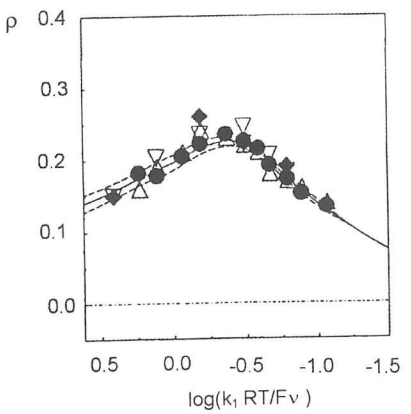
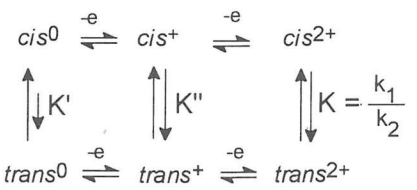


Fig. 3 - Experimental (symbols) and theoretical (lines) variations of $\rho = i_p(trans^{+/0})/i_p(cis^{0/+})$ as a function of scan rate (ν) and concentration (•, 0.95 mM; Δ, 2.0 mM; ∇, 2.6 mM; ♦, 0.96 mM) at 273 K. The working curve was determined for $k_1 = 5.6\ s^{-1}$ and $k_2/k_1 = 0.18$ (dashed lines, $k_2/k_1 = 0.19$ and $k_2/k_1 = 0.17$, for comparison).

Although scheme 1 represents the only sequence that is compatible with the experimental data, the most general kinetic situation that may arise is the one described by the classical form of a *double square scheme* given in scheme 2.



Scheme 2

Because $\Delta G^o = 0$ for each thermochemical cycle represented, the evaluation of the formal equilibrium constants was possible allowing us to decide if the reactions between the neutral and between the monocation isomers did not occur because of thermodynamic or kinetic reasons. Indeed, $K' = 6.9 \times 10^{-4}$ indicates that the $trans^0$ is thermodynamically unstable (*ca.* 4 kcal mol^{-1}) relative to the cis^0 isomer and therefore formation of the former can only occur under kinetic control.

According to $K'' = 1.5$, $trans^+$ is slightly more stable (*ca.* 0.2 kcal mol^{-1}) than the cis^+ and a further increase of stability of the *trans* isomer occurs upon oxidation ($K = k_1/k_2 = 5.6 \Rightarrow \Delta G^o = -0.9$ kcal mol^{-1}).

However, due to the experimentally observed high stability of the cis^+ and $trans^+$ species the isomerization activation barrier should be sufficiently high to prevent isomerization at this level, but decreases dramatically upon the following oxidation with the concomitant increase in structural lability.

Several examples of electron-transfer induced *cis*/*trans* isomerization have been reported, in particular for $[Mo(CO)_2(dmpi)_4]$ (dmpi = 2,6-dimethylphenyl isocyanide) [4] and $[Cr(CO)_2(dppe)_2]$ [5], as well as for $[Ru(S_2CNEt_2)_2(PPh_3)_2]$ [6]. However, the isomerizations take place only as the result of single-electron oxidation processes and according to a simple square-scheme mechanism.

This work provides the first detailed kinetic and mechanistic study of the involved isomerization reactions induced by electron-transfer in a d^6 rhenium-phosphine complex, with the relevant feature that although a single electron oxidation of the *cis*-isomer can lead to a high increase of the relative thermodynamic stability of the corresponding *trans vs.* the *cis* isomer, kinetic effects require a second oxidation step to allow a significant *cis* to *trans* isomerization to occur.

Electrochemically induced deprotonation

of the hydride complexes $[ReClH(NCR)(dppe)_2]^+$

The rhenium(I) metal site $\{ReCl(dppe)_2\}$ presents a high π-electron releasing ability and promotes electrophilic attack at unsaturated organic ligands such as isocyanides [7], nitriles [8], alkyne-derived allene [9] and vinylidene [10]. However, while at the ligating C-ligand the electrophilic addition appears to be regioselective occurring at the β-position relative to the metal, at the analogous complexes with nitriles (which are weaker π-acceptors) the protonation is observed either at the ligand or at the metal (which is then expected to be more electron-rich than in the other cases).

The electrochemical behaviour of the hydride complexes has been studied by CV in the scan rate range of 300 - 0.05 V s^{-1} at Pt disc electrodes in thf or CH_2Cl_2 solutions [11]. Typical cyclic voltammograms for these species are depicted in Fig. 4.

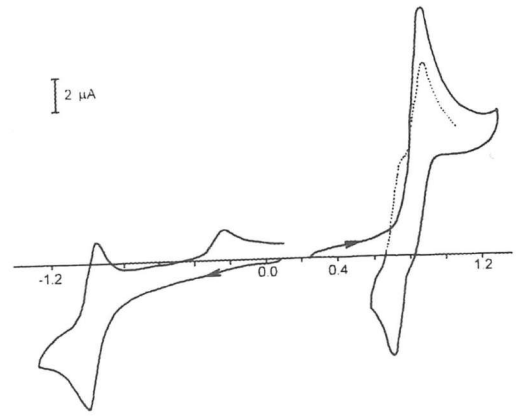


Fig. 4. Cyclic voltammograms for 0.6 mM $[ReClH(NCC_6H_4Cl)(dppe)_2]^+$ in CH_2Cl_2 with 0.2 M $[NBu_4][BF_4]$. ν = 100 mV s^{-1}.

These complexes undergo anodic and cathodic processes which are partially reversible at low scan rates, the anodic one tending to a two-electron process, upon CPE, with proton loss as indicated by acid-base titration of the electrolysed solution. A pronounced increase of chemical reversibility is observed upon increasing the scan rate.

It is noteworthy to mention that an increase of the concentration of the hydride complex results in an increase of the scan rate required to achieve chemical reversibility in oxidation thus clearly indicating a reaction order higher than one in the rhenium complex.

Moreover, as a result of the cathodic reduction (or the anodic oxidation) of the hydride complexes another species is formed, as detected by the corresponding new waves. The same set of waves was detected for the species chemically obtained upon addition of a base such as $[NBu_4]OH$ to a solution of the hydride complex. According to IR, NMR and elemental analysis, that species was shown to be the nitrile complex *trans*-$[ReCl(NCR)(dppe)_2]$.

Therefore, the deoxidised form of the *trans*-nitrile complex is the product formed in the time scale of cyclic voltammetry while upon an exhaustive 2 faraday/mol anodic CPE of the hydride complex decomposition products are obtained. In addition, the neutral form of the *trans*-nitrile complex was obtained upon cathodic CPE.

The anodically induced deprotonation of the hydride complexes were studied by simulation of the voltammograms at different scan rates and concentrations of the starting complex.

An almost perfect agreement between the experimental and the simulated voltammograms was obtained upon assuming not a classical ECE but a DISP2-type [12] mechanism of the type shown in scheme 3 where the oxidation of the oxidised rhenium nitrile complex *trans*-$[ReCl(NCR)(dppe)_2]^+$ (here denoted by Re^+) is performed homogeneously, by electron-transfer to ReH^{2+} rather than by the electrode.

$$ReH^+ - e \rightleftharpoons ReH^{2+}$$

$$ReH^{2+} + B \overset{K}{\rightleftharpoons} Re^+ + HB^+$$

$$Re^+ + ReH^{2+} \xrightarrow{k} Re^{2+} + ReH^+$$

Scheme 3

Owing to the steady-state chemical behaviour of the Re^+ species, the simulations could not afford the independent values of K and k but only the apparent rate constant, $k_{ap} = kK[B]/[HB^+]$, which was shown to increase with the basicity of the medium as indicated in Table 2.

Although the mechanism for the cathodic process could not be established since the exact determination of the chemical reversibility of this wave was critically dependent on the experimental conditions, it was observed that the basicity of the medium had no effect on the cathodic process of the hydride complexes. Moreover, it can be stressed that dehydrogenation occurs upon reduction.

Table 2 - Effect of the basicity of the electrolyte solution media on the apparent rate constant, k_{ap}.

Medium	$k_{app} = \frac{k.K.[B]}{[HB^+]}$ ($dm^3\ mol^{-1}\ s^{-1}$)
CH_2Cl_2	100
thf	250
thf + pyridine	400

The electrochemistry of metal hydrides has been a matter of current interest and shown to involve, *e.g.*, anodically induced H^+ extrusion [13,14], cathodically induced H_2 formation [14], or further reactivity such as nucleophilic attack [15].

Our study indicates that the rupture of M-H bond induced by electrochemical oxidation can involve a bimolecular process and therefore be considerably more complex than a simple intramolecular metal-hydride bond cleavage.

Electrocatalytic oxidation of biological thiols by an *Amavadine* model

Amavadine is the name given to a vanadium(IV) complex isolated from the *Amanita* mushrooms which was formulated as $[V(HIDPA)_2]^{2-}$ ($HIDPA^{3-}$ = basic form of the 2,2'-(hydroxyimino)-dipropionic acid, $HONCH(CH_3)COOH$), on the basis of the molecular structure of its model $[V(HIDA)_2]^{2-}$ ($HIDA^{3-}$ = basic form of the N'-(hydroxyimino)-diacetic acid, $HONCH_2COOH$), as established by an X-ray diffraction analysis [16]. However, the biological function of *Amavadine* has not yet been elucidated although some evidence suggests it can be involved in some kind of electron transfer process.

Indeed, these *Amavadine* models acts as electron-transfer mediators in the electrocatalytic oxidation of thiols through a Michaelis-Menten type mechanism involving the interaction of the substrate with the oxidised form of the catalyst [17]. This demonstrates, for the first time, the involvement of such mechanism in an electrocatalytic process.

In KCl aqueous solution and at a Pt-disc electrode the *Amavadine* models undergo a single-electron reversible oxidation corresponding to the V(IV) → V(V) conversion and act as mediators in the electrocatalytic oxidation of thiols, in particular cysteine [$HSCH_2CH(NH_2)COOH$], mercaptoacetic acid ($HSCH_2COOH$) and mercaptopropionic acid [$HS(CH_2)_2COOH$].

The catalytic nature of the anodic waves is evident from the enhancement of the anodic peak current upon the addition of increasing amounts of thiol for which, in the absence of the vanadium system, no direct anodic oxidation has been detected (Fig. 5, where γ is defined as the ratio between the substrate and the catalyst concentrations [S] / [M]).

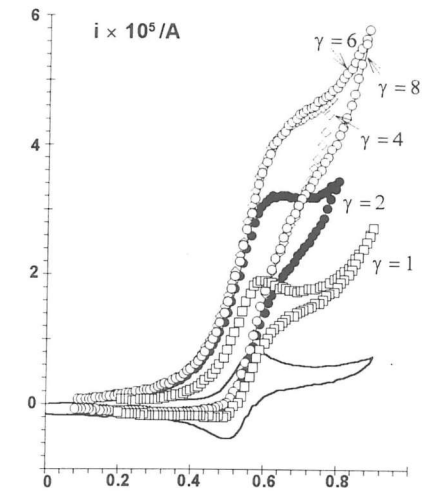


Fig. 5 - Cyclic voltammograms for the $[V(HIDA)_2]^{2-}$ complex (solid line) and for this vanadium complex/$HS(CH_2)_2COOH$ system (symbols). ν = 200 mV s^{-1}.

Moreover, the preparative electrocatalytic oxidation of each of the thiols afforded the dimers resulting from the loss of H^+ and S-S coupling, with a consumption of a number of faradays/mol correspondent to the sum of moles of vanadium complex and of thiol in solution.

The dramatic suppression effect of the increase of the catalytic activity of the mediator by a relatively high thiol concentration (Fig 6) and the fact that there is no saturation effect with the scan rate for any value of γ (Fig. 7), indicates that the simple EC catalytic mechanism is not operating.

Moreover, a complicated redox catalysis involving a progressive quenching of the mediator by formation of a stable product with the activated substrate is not operative since this would imply a saturation of the catalytic effect with both the scan rate and the concentration.

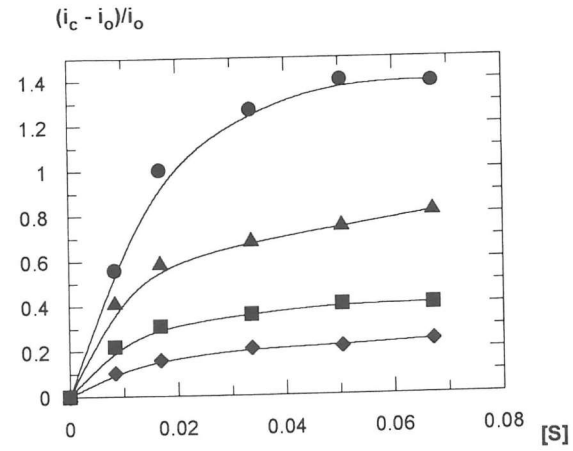


Fig. 6 - Plot of the normalised peak current $(i_c - i_o)/i_o$ *vs.* the substrate concentration [S], for the $[V(HIDA)_2]^{2-}$ /$HS(CH_2)_3COOH$ system. Scan rate of 0.05 (●), 0.1 (Δ), 0.2 (■) and 0.4 (♦) V s^{-1}.

[S] in M. Concentration of the HIDA complex, c = 8.4 mM.

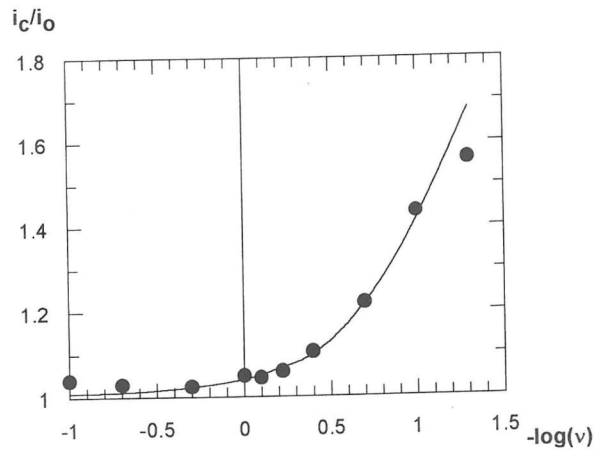
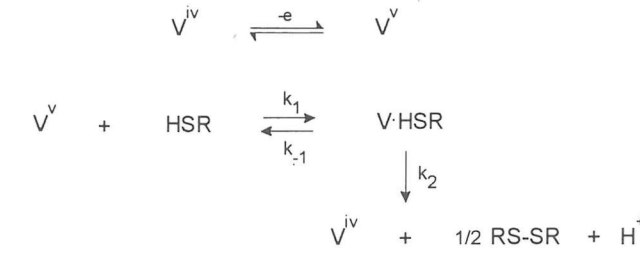


Fig. 7 - Plot of experimental (symbol) and simulated (line) i_c/i_o *vs.* -log(ν), for excess factor $\gamma = 1$ (ν in V s^{-1}).

Therefore, the experimental data are reminiscent of the classical Michaelis-Menten enzymatic kinetics, with the oxidation of the thiol by the oxidised vanadium species proceeding *via* the transient formation of an adduct between the V^v species and the thiol as described in scheme 4.



Scheme 4

In such a situation, small values of the thiol concentration lead to a process limited by the slow reaction of the V^v complex with the thiol leading to the observation of the classical kinetic behaviour for redox catalysis. Increasing the thiol concentration, progressively shifts the kinetic control of the regeneration process to the decomposition of the transient adduct.

The detailed mechanism of this redox catalysis process has been investigated by using a CV simulation programme and the best fit was obtained for $k_1 = 1.2 \times 10^3$ M^{-1} s^{-1}, $k_2 = 2.5$ s^{-1} and $k_{-1} << k_2$.

This work demonstrated for the first time the involvement of a Michaelis-Menten enzymatic type mechanism in redox catalysis and also gives some support to the hypothesis [18] that *Amavadine* is conceivably involved in some kind of protective/defensive system of the mushrooms by specific oxidation of the thiols to give disulphide bridges as a possible way of cross-linking protein fibre for the regeneration of the tissues.

Acknowledgements

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