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# Molecular Catalysis of Electrochemical Reactions: Competition between Reduction of the Substrate and Deactivation of the Catalyst by a Cosubstrate. Application to N<sub>2</sub>O Reduction.

Rana Deebea,<sup>[a]</sup> Sylvie Chardon-Noblat<sup>[a]</sup> and Cyrille Costentin<sup>\*,[a,b]</sup>

[a] Prof. Dr. C. Costentin, Dr. S. Chardon-Noblat, R. Deebea  
Univ Grenoble Alpes, DCM, CNRS, 38000 Grenoble, France  
E-mail: cyrille.costentin@univ-grenoble-alpes.fr

[b] Prof. Dr. C. Costentin  
Université de Paris, 75006 Paris, France

Supporting information for this article is given via a link at the end of the document.

## To the memory of Prof. Jean-Michel Savéant

**Abstract:** In the context of molecular catalysis of electrochemical reactions, the competition between reduction of the substrate and deactivation of the catalyst by a cosubstrate is investigated. It is a frequent situation because proton donors are ubiquitous cosubstrate in reductive electrochemical reactions and molecular catalysts, either transition metal complexes or organic aromatic molecules, are often prone to electrohydrogenation. We provide a formal kinetic analysis in the framework of cyclic voltammetry and we show that the response is governed by two parameters and that the competition does not depend on the scan rate. From this analysis a methodology is proposed to analyze such systems and then illustrated via the study of N<sub>2</sub>O to N<sub>2</sub> electroreduction catalyzed by 4-cyanopyridine in acetonitrile electrolyte with water as proton donor. Incidentally, new insights into the mechanism of 4-cyanopyridine radical anion protonation are revealed.

## Introduction

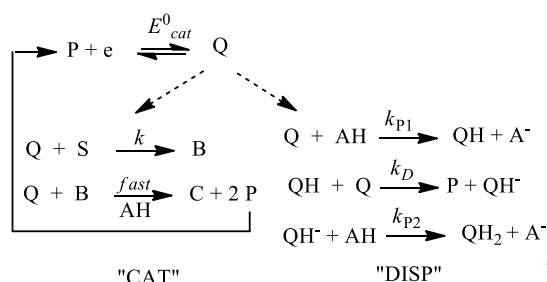
Mediated electrochemical reactions are currently experiencing a large interest due to the revival of organic electrochemistry<sup>1</sup> and the intense activity in small molecules activation in relation with conversion of electricity to fuels.<sup>2</sup> In both fields, primary focus is on the development of efficient and, if applicable, selective chemical catalysts. However another important figure of merit is the durability of the catalyst which is often limited by a deactivation process of the catalyst and not widely discussed. The problem of catalyst deactivation is a key issue in homogeneous catalysis<sup>3</sup> and has also been a subject of interest in molecular catalysis of electrochemical reactions for a long time.<sup>4</sup> Chemical evolution of a designed molecular catalyst may result to various situations with divergent consequences ranging from a dead-end of the catalytic process (chemical transformation of the active form of the catalyst to a non active molecule) to acceleration of catalysis (chemical transformation of the precursor or/and active catalyst to a more active form) or transformation of molecular catalysis to electrocatalysis process via electrodeposition of an active catalytic species on the working electrode surface, metallic for example.<sup>5</sup> The latter may in particular be encountered when low valent transition metal complexes are used as catalysts, often designed with ligands relieving the reduced metal electronic density, subjected to

chemical transformation under harsh electrochemical conditions, e.g. very negative potentials or acidic conditions for reductions. Because most electrochemical reductions require protons as cosubstrates, possible protonation of one of the ligands inducing complex demetallation is indeed often a deleterious pathway for molecular catalysis, although it may sometimes be beneficial.<sup>6,7</sup> Even if protonation of the ligand does not lead to demetallation, it may open the way to the corresponding hydrogenated complex formation (2e<sup>-</sup>-2H<sup>+</sup> process) which can result in a less efficient or a non active molecule. The situation is similar in the case of organic molecules as catalysts which may act as outersphere electron donors.<sup>8</sup> These redox catalysts are indeed often aromatic molecules with conjugated systems prone to electro-assisted hydrogenation via addition of two electrons and two protons. Catalyst deactivation has been studied in redox catalysis in the framework of a substrate / activated catalyst addition inhibition pathway,<sup>4</sup> but the competition between catalysis and deactivation of the catalyst due to reaction with the cosubstrate, a proton donor for instance, has not yet been addressed. Due to its ubiquity, it is interesting to investigate this question, so as to know the operational parameters controlling the competition. Herein we address this issue using cyclic voltammetry (CV) as an analytical tool. Softwares are currently available to simulate CVs and they proved to be very useful. However, a formal kinetic analysis is helpful to establish the parameters controlling the CV response, to identify limiting cases and get guess values of the governing rate constants within restrictive simplifications such as steady state approximation for intermediates (pure kinetics conditions). Then digital simulations can be performed to check the consistency of the determined constants with the approximation made for their evaluation. Therefore we first performed formal kinetic analysis. We propose this analytical approach before performing CV simulations because, from our point of view, it avoids simulation errors and blind testing. Here we report the corresponding results and we use the reduction of N<sub>2</sub>O to N<sub>2</sub> mediated by 4-cyanopyridine in acetonitrile electrolyte with water as a proton donor as a methodological illustrating example.

## Results and Discussion

### Formal kinetic analysis

We consider a Nernstian redox couple P/Q as a homogeneous catalyst for the two electron transformation of a substrate S. For the sake of simplicity we consider only one possible pathway for the catalytic process, namely an ECCE' in which the first chemical step is rate determining (rate constant  $k$ ), the second chemical step is fast and involves AH as cosubstrate and the second electron transfer ( $E'$ ) is homogeneous (scheme 1).<sup>9</sup> Such a mechanism is at work for example in the case of CO<sub>2</sub> reduction with iron porphyrins as catalyst,<sup>10</sup> or N<sub>2</sub>O reduction with organic molecules as catalysts.<sup>11</sup> Adaptation to other mechanisms<sup>9</sup> is possible but considering all possibilities would lead to a tedious study ending to a taxonomic nightmare. The electrochemical generation of the reduced form of the catalyst Q makes it a more basic species than the initial form P. Therefore a competition occurs in the diffusion reaction layer between the reaction of Q with the substrate S, assumed to be in large excess, and its protonation by a proton donor AH, assumed to be in large excess as well. The protonated catalyst QH is reduced in solution (DISP)<sup>12</sup> and finally protonated a second time (scheme 1).



**Scheme 1.** Mechanism for competition between catalysis (CAT) and catalyst hydrogenation (DISP). Catalyst redox couple: P/Q; P: oxidized form, Q: reduced form; QH: protonated form of Q; QH<sup>-</sup>: reduced form of QH; QH<sub>2</sub>: hydrogenated catalyst; S: substrate, B: intermediate; C: product; AH: acid; A<sup>-</sup>: conjugated base

QH can also be reduced at the electrode surface but we restrict our analysis to the case where protonation of Q is not too fast so that QH is not produced close to the electrode surface. A very fast protonation of Q would make it an inefficient and hence useless catalyst. The competing situation is referred to as CAT-DISP mechanism. Note that the first protonation (rate constant  $k_{P1}$ ) is assumed to be irreversible due to a large driving force considering that reduction of P into Q makes Q basic and because of the fast following-up reduction of QH. The first protonation step is assumed to be the rate determining step of the DISP pathway. Finally we assume that pure kinetics are achieved owing to fast catalysis compared to the timescale of CV, a condition readily achieved in many practical cases. Combined with the large excess of both substrate (S) and cosubstrate (AH), this leads to canonical conditions corresponding to a characteristic steady-state S-shaped CV in the absence of competing catalyst protonation.<sup>9</sup> The corresponding CV equation is:

$$\psi = \frac{i}{FSC_{cat}^0 \sqrt{D \frac{Fv}{RT}}} = \frac{\sqrt{\frac{RT}{Fv}} \sqrt{2kC_S^0}}{1 + \exp\left[\frac{F(E - E_{cat}^0)}{RT}\right]} = \frac{\sqrt{2\lambda_{cat}}}{1 + \exp(-\xi)} \quad (1)$$

where  $C_{cat}^0$  and  $C_S^0$  are the concentrations of the catalyst and the substrate respectively,  $E_{cat}^0$  is the standard potential of the catalyst,  $E$  is the electrode potential,  $i$  is the current,  $k$  is the rate constant of the catalytic rate determining step,  $v$  is the scan rate,  $S$  is the electrode surface area,  $D$  is the diffusion coefficient,  $R$  is the gas constant,  $F$  is the Faraday constant,  $T$  is the temperature and  $\xi = -F(E - E_{cat}^0)/RT$  is the dimensionless potential. Alternatively, in the absence of substrate, a large concentration of acid and fast protonation leads to an irreversible two electron wave corresponding to an DISP mechanism in pure kinetics conditions with peak currents and potentials being:<sup>12</sup>

$$\psi_p = \frac{i_p}{FSC_{cat}^0 \sqrt{DFv/RT}} = 0.992 \quad (2)$$

and

$$\xi_p = -\frac{F(E_p - E_{cat}^0)}{RT} = 0.78 - \frac{1}{2} \ln\left(\frac{RT}{2Fv} k_{P1} C_{AH}^0\right) \quad (3)$$

In between these two limiting cases, as shown in the Supporting Information (SI), the CV response is governed by two

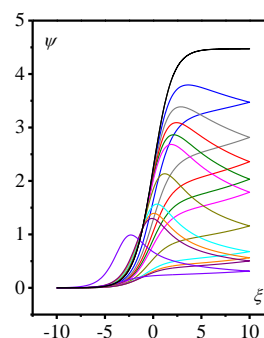
dimensionless parameters,  $\lambda_{cat} = \frac{kC_S^0}{Fv/RT}$  and  $\lambda_p = \frac{k_{P1}C_{AH}^0}{Fv/RT}$ , which can be replaced by a combination of both:

$$\rho = \frac{\lambda_p}{\lambda_{cat}} = \frac{k_{P1}C_{AH}^0}{kC_S^0}, \quad \rho \text{ thus being the dimensionless parameter}$$

gauging the competition. The corresponding CV equation is:

$$\frac{\psi}{\sqrt{2\lambda_{cat}} \sqrt{1+\rho}} \left[ 1 - \frac{1}{2\left(1+\frac{1}{\rho}\right)} + \exp(-\xi) \right] + \frac{1}{2\left(1+\frac{1}{\rho}\right)} I_\psi = 1 \quad (4)$$

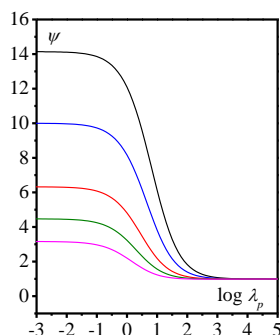
$I_\psi$  is the integral of the current convoluted with diffusion (see SI). Note that the dimensionless current  $\psi = i / FSC_{cat}^0 \sqrt{DFv/RT}$  can be easily replaced by the more common  $i/i_p^0 = \psi/0.446$  quantity where  $i_p^0$  is the peak current corresponding to the catalyst alone in absence of proton donor. Typical CVs showing the transition between the two limiting behaviors upon increasing  $\lambda_p$  (or  $\rho$ ) for a given value of  $\lambda_{cat}$  are plotted in figure 1 via numerical resolution of equation (4) (see SI for details).



**Figure 1.** Dimensionless CVs for a CAT-DISP mechanism with  $\lambda_{cat} = 10$  and various values of the competition parameter  $\rho = 0$  (black), 0.04 (blue), 0.084

(grey), 0.12 (red), 0.16 (green), 0.2 (magenta), 0.4 (dark yellow), 1 (cyan), 1.5 (orange), 2 (purple),  $10^3$  (violet).

It is seen that a convenient way to evaluate the position of the system, i.e.; the competition between catalysis and catalyst deactivating hydrogenation, is to look at the peak current as function of  $\lambda_p$ . Such plots are shown in figure 2 for various values of  $\lambda_{cat}$ . Alternatively, the calculated curves (obtained from numerical resolution of equation (4)) can be plotted as the peak current as function of  $\rho$  (figure S1).



**Figure 2.** Variation of the catalytic current for a CAT-DISP mechanism with the kinetic parameter  $\lambda_p$  for various values of the parameter  $\lambda_{cat} = 100$  (black), 50 (blue), 20 (red), 10 (green), 5 (magenta).

These calculated curves can be used to analyze experimental data. Starting with a solution with no (or little amount of) proton donor and excess of substrate, the catalytic plateau current can in principle be obtained, thus giving the value of  $\lambda_{cat}$ , and therefore of the rate constant  $k$ . With this value in hands, it is possible to choose the adequate working curve. Then, the dimensionless peak currents measured at various concentration of added proton donor can be adjusted on the adequate calculated curve, thus giving the corresponding  $\lambda_p$  value from

which an apparent pseudo first order rate constant,  $k_p^{ap}$ , is

obtained:  $\lambda_p = \frac{k_p^{ap}}{Fv/RT} \cdot k_p^{ap}$  can be used to get insights into

the catalyst hydrogenation mechanism. If the protonation is first order, as in the tutorial reaction scheme considered here, then  $k_p^{ap}$  is proportional to  $C_{AH}^0$ . If not, then the reaction order in AH

can be obtained from the variation of  $k_p^{ap}$  with  $C_{AH}^0$ . Of course, the same kinetic information can in principle be obtained by the direct study of the catalyst's hydrogenation in the absence of substrate where reduction of the substrate may vary from a one electron reversible wave at low AH concentration to an irreversible two electron wave in the presence of large AH concentration. In the present analysis, the information on the catalyst's hydrogenation is retrieved from a kinetic competition between the protonation step of the reduced catalyst and the homogeneous reduction of the substrate by the reduced catalyst species whereas it is obtained from competition between the protonation step of the reduced catalyst and diffusion in the direct analysis. Hence, scan rate can modulate the competition

in the latter case which is governed by  $\lambda_p = \frac{k_p^{ap}}{Fv/RT}$  but scan rate has no effect in the former case, provided the system

remains in pure kinetics conditions, where the competition is

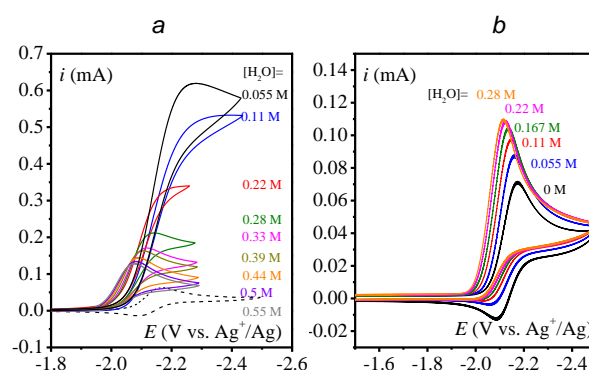
governed by  $\rho = \frac{k_p^{ap}}{kC_S^0}$ .

It is worth noting that the calculated theoretical curves have been obtained considering several simplifying assumptions, namely excess of S and AH, pure kinetics conditions and only the DISP pathway for the catalyst's hydrogenation. It is therefore recommended to check the consistency of the analysis via digital simulation of the whole process using as guess parameters those obtained from the above methodology. The proposed methodology consisting in using the simple analytical approach prior running CV simulations avoids performing blind error and trial simulations.

#### Nitrous oxide reduction catalyzed by 4-cyanopyridine in the presence of water

Nitrous oxide ( $N_2O$ ) is a greenhouse gas not only responsible for 4% of the additional greenhouse effect observed since the start of the industrial era<sup>13</sup> but also being the main contributor to the destruction of the ozone layer of the 21<sup>st</sup> century.<sup>14</sup> It is therefore interesting to find ways to efficiently reduce  $N_2O$  into inert  $N_2$ . Doing so, we recently investigate the catalysis of the electrochemical reduction of  $N_2O$  in acetonitrile electrolyte with rhenium and manganese complexes<sup>15</sup> but also organic molecules (anthracene, perylene...) as homogeneous catalysts.

In this latter case we have shown that they behave as redox catalysts, i.e. the catalytic process undergoes a rate determining outersphere electron transfer from the electrogenerated radical anion of the catalyst to  $N_2O$ . It was observed that addition of water as proton donor did not improve the catalytic current indicating that the outersphere rate determining step is not coupled to proton transfer. Because the organic catalysts we used are known to be subjected to electrohydrogenation upon reduction in the presence of a proton source,<sup>16</sup> based on the above analysis, we can infer that the rate for protonation with water for concentration up to 0.5 or 1 M is much smaller than the catalytic rate constant. On the contrary, with 4-cyanopyridine as redox catalyst, we observe a deleterious effect of addition of water on the catalytic current (figure 3a).



**Figure 3.** CVs of 4-cyanopyridine in acetonitrile with  $n\text{-Bu}_4\text{NPF}_6$  (0.1 M) on a 3 mm diameter glassy carbon electrode.  $v = 0.1$  V/s. (a) 1.45 mM under  $N_2O$  with increasing additional amount of water (concentrations are given on the CVs).

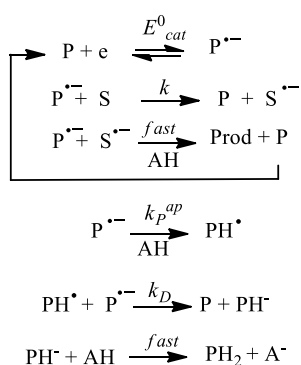
We attribute this effect to a deactivation process of the catalyst via reaction of water with 4-cyanopyridine radical anion competing with electron transfer to  $N_2O$ . This hypothesis is supported by the observation that the reduction of 4-



cyanopyridine is only partially chemically reversible in acetonitrile, which contains a substantial residual amount of water, and becomes fully irreversible and bielectronic upon addition of water (figure 3b). We thus analyze the data according to the above described methodology in the framework of the CAT-DISP competition (scheme 2). The choice of the DISP pathway for the catalyst electro-assisted hydrogenation will be justified a posteriori. From the CVs recorded under  $N_2O$  without added water at different scan rates (figure S2), the current is

plateauing and corresponds to  $\lambda_{cat} = \frac{k_{cat}}{Fv/RT} = 13$  with  $k_{cat}$

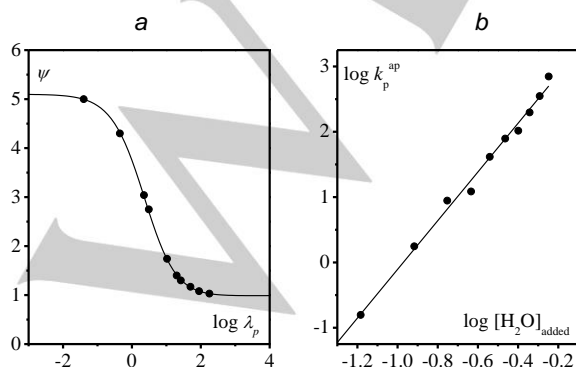
being the pseudo-first order rate constant for outersphere electron transfer from 4-cyanopyridine radical anion to  $N_2O$ . Then, the experimental dimensionless peak currents measured at different addition of water are reported on the curve numerically calculated for  $\lambda_{cat} = 13$  as in figure 2 (figure 4a).



**Scheme 2.** Mechanism CAT-DISP of reduction of  $N_2O$  (substrate, S) into  $N_2$  (product, Prod) with 4-cyanopyridine (initial reduced form of the redox couple, P) in the presence of water (proton donor, AH).

From this plot, the value of  $k_P^{ap}$  is obtained for each concentration of water (figure 4b). With these values in hand, the ECE-DISP competition parameter,<sup>12</sup>  $\frac{k_D}{k_P^{ap3/2}} C_{cat}^0 \sqrt{\frac{Fv}{RT}}$ , can be

evaluated to check on whether or not it is justified to assume that  $\text{PH}^{\bullet}$  is reduced in solution (DISP) rather than at the electrode surface (ECE). Considering a lower limit for the homogeneous reduction rate constant as being  $k_D = 10^8 \text{ M}^{-1}\text{s}^{-1}$ , the competition parameter remains larger than  $10^2$  thus validating the hypothesis of the prevalent DISP pathway.<sup>12</sup> The consistency of the whole analysis was finally checked by digital simulation of the CVs under  $N_2O$  (figure S3).



**Figure 4.** Catalysis of  $N_2O$  reduction with 4-cyanopyridine as catalyst in the presence of water. (a) Peak current (dots) adjusted on the CAT-DISP working curve corresponding to  $\lambda_{cat} = 13$ . (b) Variation of the apparent protonation rate constant as function of added water.

Interestingly, from the slope of the  $\log k_P^{ap}$  vs.  $\log [\text{H}_2\text{O}]$  plot, we observe that the reaction order in water is ca. 4. This suggests that the protonation of the radical anion occurs via a cluster of water molecules. Up to four molecules of water have to be associated to the radical anion for the proton transfer to occur irreversibly. It is reminiscent of the observation made for the concerted electron-transfer to superoxide in acetonitrile in the presence of water.<sup>17</sup> This result emphasizes the peculiar behavior of proton. This example also illustrates how mechanistic information can be gathered from the competition between two different chemical processes, catalysis and hydrogenation of the catalyst.

## Conclusion

We have investigated the competition between reduction of the substrate and deactivation of the catalyst by a cosubstrate for molecular catalysis of electrochemical reactions. The formal kinetic analysis in the framework of cyclic voltammetry in pure kinetics conditions and excess of substrate and cosubstrate shows that the system is governed by two parameters and that the competition does not depend on scan rate. Theoretical curves for variation of the current as function of the governing parameters have been provided. A methodology is proposed to analyze such systems using the working curves. This methodology has been successfully applied to the electroreduction of  $N_2O$  to  $N_2$  electroreduction catalyzed by 4-cyanopyridine in acetonitrile electrolyte with water as proton donor. This provides, as a side result, the interesting observation that the protonation of 4-cyanopyridine radical anion protonation with water requires the association of four water molecules.

We hope that such analysis can serve in the future for a better understanding of molecular catalyst deactivation, a common limitation in the use of molecular catalysts for small molecule activation in the framework of contemporary energy challenges or for organic transformations.

## Experimental Section

See Supporting Information.

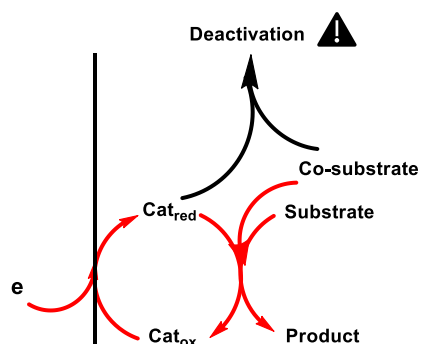
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**Keywords:** Molecular Catalysis • Cyclic Voltammetry • Catalyst Deactivation • Nitrous Oxide Reduction • Electrocatalysis

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## Entry for the Table of Contents



Homogeneous catalysis of electrochemical reactions allows overcoming overpotential encountered in direct reduction or oxidation. The competition between reduction of the substrate and deactivation of the catalyst by a cosubstrate is however often source of the low durability of catalysts. This issue is analysed in the framework of cyclic voltammetry and it is illustrated by the reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  catalysed by 4-cyanopyridine in the presence of water.

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