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Importance of Ligand Exchange in the Modulation of Molecular Catalysis. Mechanism of the Electrochemical Reduction of Nitrous Oxide with Rhenium Bipyridyl Carbonyl Complexes.

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ABSTRACT: Molecular catalysis of electrochemical reactions involving transition metal complexes as catalysts requires getting a free metal coordination site to bind the substrate. It implies that the generation of a strong coordinating ligand as product or co-product of the reaction might be detrimental for an efficient catalysis because it can bind the metal center and block or slow down the catalytic process. This self-modulation phenomenon is revealed and illustrated via a thorough spectro-electrochemical investigation of the mechanism of the electrochemical reduction of nitrous oxide with rhenium bipyridyl triscarbonyl complexes $[Re(bpy)(CO)_3X]^{n+}$ (X = CH₃CN, Cl⁻, n = 0 or 1) as catalyst. We show that the bi-reduced $[\text{Re}^{\circ}(\text{bpy}^{\bullet})(\text{CO})_3]^-$, electrogenerated from $[\text{Re}(\text{bpy})(\text{CO})_3X]^{n+}$, readily reacts with N₂O and produces the hydroxo complex [Re¹(bpy)(CO)₃(OH)]. Because hydroxide, a product of the reaction, is a stronger coordinating ligand than acetonitrile or chloride, catalysis does not occur significantly at a potential where $[\text{Re}^{\circ}(\text{bpy}^{\bullet})(\text{CO})_3]^-$ is generated from $[\text{Re}(\text{bpy})(\text{CO})_3X]^+$. Substantial catalysis is only triggered at a potential corresponding to the second reduction of [Re^I(bpy)(CO)₃(OH)]. Nonethe less, we show that a slower innersphere reduction of N₂O by the monored $[Re^{I}(bpy^{\bullet-})(CO)_{3}X]^{(n-1)+}$ (X = CH₂CN, Cl⁻) occurs due to the lability of acetonitrile and chloride in these species. Because hydroxide is less labile and cannot be displaced to create an open coordination position for N₂O, only an even slower outersphere reduction of N₂O by the monoreduced $[Re^{1}(bpy^{-})(CO)_{3}(OH)]^{-}$ takes place. However, we finally show that an excess of free chloride is able to displace hydroxide and then open the way for a faster innersphere process. This remarkable example emphasizes the critical role of ligand exchange in modulating molecular catalysis of electrochemical reactions with transition metal complexes as catalysts, a likely general phenomenon.

Keywords: Molecular Catalysis, Nitrous Oxide, Electrochemistry, Mechanism, Self-modulation

Introduction

Molecular catalysis of electrochemical reactions often involves transition metal complexes as catalysts due to their ability to bind and activate the substrate to be transformed. The current intense activity in the field of small molecules activation, in particular reduction of protons, ¹ O₂, ² CO₂ ³ or more recently N2⁴, offers a myriad of examples. A common feature of such processes is the necessity to get a free metal coordination site allowing the substrate to bind. The corollary is thus that among the various steps of such a catalytic process, ligand exchanges at the metal center are involved, often triggered by variation of the metal oxidation state. One consequence is that the formation of a reaction product or co-product being a strong coordinating ligand might bind the metal and then block the regeneration of a free coordination site required to sustain catalysis. The homogeneous electrochemical reduction of CO₂ to CO by the molecular catalyst [Ni(cyclam)]²⁺ provides a typical example in which the rate-limiting step during catalysis is CO decoordination from the deactivated intermediate [Ni(cyclam)(CO)]⁺ as shown by Kubiak and coworkers.⁵ Even more drastic is the case N₂ splitting by electrogenerated reduced rhenium or molybdenum complexes leading to stable nitride complexes, which then would require additional overpotential to release NH₃ via three proton-coupled electron transfers .^{6,7,8,9,10,11} In other cases, catalysis is not inhibited but only self-modulated as shown for the reductive cleavage of chloroace-tonitrile catalyzed Co(I) cobalamins and cobinamides where the production of free chloride, as catalysis goes on, shifts the generation of the Co(I) active species toward more negative potentials thus slowing down catalysis.¹² Due to their ubiquity, it is of prime importance to identify and analyze these phenomena in order to fully understand catalytic processes and, more importantly, provide strategies to avoid or delay catalyst deactivation ⁵ or even design new reactions.¹³

In that context, we recently reported that rhenium carbonyl complexes catalyze nitrous oxide (N₂O) electroreduction. ¹⁴ N₂O is a greenhouse gas responsible for 4% of the additional greenhouse effect observed since the start of the industrial era. ¹⁵ Its reduction to dinitrogen is thus of interest to minimize its release in the atmosphere. Additionally, deoxygenation of N-O bonds is currently relying on thermochemical methods and sacrificial reducing agents. ¹⁶ It is thus timely to elaborate selective, clean, and energy thrifty processes for deoxygenation reactions targeting *N*-oxides. Interestingly, rhenium bipyridyl tri-carbonyl complexes able to catalyze the electrochemical reduction of N_2O have also proved to be efficient photocatalysts for pyridine N-oxide deoxygenation. ¹⁷ This suggests that an innersphere mechanism via metal-oxygen binding might be at work as opposed to an activation through a nucleophilic attack of the reduced metal to the electrophilic central nitrogen of N_2O proposed from the electronic analogy between N_2O and CO_2 . ¹⁸

We have thus investigated in detail the mechanism of N_2O electroreduction catalyzed by $[Re(bpy)(CO)_3(X)]^{n+}$ complexes (bpy= bipyridine; X = chloride, hydroxide or acetonitrile, n depends on the X ligand). These complexes are indeed known for a long time to be efficient catalysts for CO_2 to CO conversion and mechanistic studies have shown that the formation of the bi-reduced species $[Re^o(bpy^{\bullet-})(CO)_3]^-$ is required for CO_2 to bind the rhenium center and trigger catalysis. ¹⁹ This involves via loss of the X ligand to generate a free coordinated site (scheme 1). As opposed to the case of nickel cyclam complexes, after the C-O bond breaking, CO is easily released allowing regenerating the vacant site.

Scheme 1. Proposed principle for CO_2 and N_2O activation with rhenium bipyridyl carbonyl complexes. ^{18,19}



Activation of N₂O has also been proposed to be initiated by its reaction with $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ but, on the timescale of cyclic voltammetry, no substantial catalysis occurs at a potential where $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ is electrogenerated.^{14,18} This is the first result of the present work which reveals that formation of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$ is responsible for this lack of catalysis. This prompted us to investigate the role of the labile ligand in the catalytic process and uncover unexpected slower catalytic pathways but operating at a lower overpotential without requiring the generation of the bi-reduced species $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$. Kinetic analysis will show that ligand exchanges on the rhenium center will prove to be crucial in directing the reaction toward innersphere or slower outersphere pathways and hence modulate the catalysis.

Results

Chemical reduction of N_2O by electrogenerated $[Re^{\circ}(bpy^{\bullet-})(CO)_3]^-$.

Starting from [Re^I(bpy)(CO)₃Cl], a solution of the bi-reduced species [Re^o(bpy^{•-})(CO)₃]⁻ in acetonitrile is obtained by a two-step electrolysis (see Supporting Information (SI) for details). The first electrolysis is performed at -1.36 V (all potentials are given vs. SCE) and leads to the formation of a metal-bonded Re-Re dimer, [Re^o(bpy)(CO)₃]₂, as attested by the dark green color of the solution (see Figure S1). Further reduction of the dimer at -1.82 V gives the bi-reduced species [Re^o(bpy^{•-})(CO)₃]⁻ as a major product (see Figure S1). Under inert atmosphere, the electrogenerated solution of bi-reduced species (0.6 mM) is stable. [Re^o(bpy^{•-})(CO)₃]⁻ exhibits a large absorption band at 570 nm. A N₂O saturated solution of acetonitrile is then added so as to get 1.5 mM of N₂O and the evolution of the bi-reduced species is monitored in situ by UV-vis. Rapid decay is observed: half of the absorbance at 570 nm is lost after 0.5 s (Figure 1). This indicates a fast reaction between [Re^o(bpy^{•-})(CO)₃]⁻ and N₂O. The reaction can be controlled by mass transport, i.e. mixing of N₂O, but the rapid decay indicates that a lower limit of the pseudo-first order rate constant can be evaluated as $k_{ap} \approx 1.4$ s⁻¹. Therefore, for a saturated N₂O solution (i.e. $[N_2O] = 280$ mM, see SI for determination of the concentration), a lower limit of the pseudo-first order corresponding rate constant is ca. $k_{ap}^{bi} = 250 \text{ s}^{-1}$.



Figure 1. (a) Time evolution of UV-vis spectra (scans were taken every 0.5 s, l = 1 mm) of a 0.6 mM solution of electrogenerated [Re^o(bpy^{•-})(CO)₃]⁻ in CH₃CN + 0.1 M NBu₄PF₆ with addition of 1.5 mM of N₂O. Spectra in light magenta: from t = 0 (addition) to 2.5 s. Spectra for t < 0 are in purple and t > 2.5s are in red. (b) Time evolution of the absorbance at 570 nm characteristic of [Re^o(bpy^{•-})(CO)₃]⁻ absorption.

An IR spectrum was collected few minutes after the addition of N₂O to the bi-reduced species (Figure 2a) and reveals that a mixture of $[\text{Re}^{l}(\text{bpy}^{\bullet-})(\text{CO})_{3}(\text{OH})]^{-}$ and $[\text{Re}^{l}(\text{bpy})(\text{CO})_{3}(\text{OH})]$ is obtained. This conclusion was obtained from comparison of the IR spectra of authentic samples of $[\text{Re}^{l}(\text{bpy})(\text{CO})_{3}(\text{OH})]$ and $[\text{Re}^{l}(\text{bpy}^{\bullet-})(\text{CO})_{3}(\text{OH})]^{-}$ gathered from a synthesized $[\text{Re}^{l}(\text{bpy})(\text{CO})_{3}(\text{OH})]$ complex (Figure 2b and Figure S₃). Cyclic voltammograms (CV) recorded after the addition of N₂O shows a reversible system with a standard potential of -1.43 V as well as a new irreversible wave at ca. -2 V (Figure 2c). The reversible wave matches the redox behavior of the synthesized [Re¹(bpy)(CO)₃(OH)] complex (Figure S₃). ²⁰ Successive application of an oxidative potential at -1.22 V and then a reductive potential at -1.52 V to the final solution with UV-vis and IR characterization after each steps shows identical features (Figure 2d) of authentic samples of [Re¹(bpy)(CO)₃(OH)] and [Re¹(bpy⁺)(CO)₃(OH)]⁻ respectively (Figure 2b) further confirming the formation of both species upon addition of N₂O to [Re^o(bpy⁺⁻)(CO)₃]⁻.



Figure 2. (a) Ex-situ IR spectrum of $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ o.6 mM in CH₃CN + o.1 M NBu₄PF₆ before (purple) and after (red) addition of 1.5 mM of N₂O. (b) IR spectrum of $[\text{Re}^{1}(\text{bpy})(\text{CO})_3(\text{OH})]$ (red) and $[\text{Re}^{1}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$ (orange) in CH₃CN + o.1 M NBu₄PF₆. (c) CV of a solution of $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ o.6 mM after addition of 1.5 mM of N₂O in CH₃CN + o.1 M NBu₄PF₆ at o.1 V/s on a 3 mm-diameter GCE (d) Ex-situ IR spectrum of a $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ o.6 mM + 1.5 mM N₂O solution after exhaustive oxidative electrolysis at -1.22 V (red) and then exhaustive reductive electrolysis at -1.52 V (orange).

We thus propose the reaction scheme depicted in scheme 2a with consideration that the second step might not be completed. Moreover, the source of water is assumed being the residual water contained in acetonitrile. The key conclusion at this stage is that the bi-reduced species is indeed able to quickly react with N₂O. However, as observed on the cyclic voltammogram of [Re(bpy)(CO)₃Cl] under N₂O (Figure 3), at a potential where [Re°(bpy•-)(CO)₃]⁻ is generated (second wave), there is no substantial catalysis, the wave

corresponding to a maximum of 1.5 electron per rhenium center as attested by linear scan voltammetry on a rotating disk electrode (Figure 3c). Our results reveal that the reason for lack of efficient catalysis is that the labile position is coordinated by hydroxide after the first turnover (equation (1) in scheme 2). Although [Re^I(bpy)(CO)₃(OH)] is reduced at this potential, either at the electrode or in solution by [Re^o(bpy^{•-})(CO)₃]⁻ (equation (4) and (2) respectively in scheme 2b), hydroxide is partially decoordinated and released in solution on the timescale of CV.

Scheme 2.

a) Reaction between N₂O and [Re^o(bpy^{•-})(CO)₃]⁻ in solution



b) Electrochemical reduction of N_2O in the presence of $[Re^{1}(bpy^{\bullet-})(CO)_3C1]^{-1}$



$$\underbrace{ \left(\begin{array}{c} N \\ N \end{array} \right)}_{CO} \underbrace{ \left(\begin{array}{c} CO \\ CO \end{array} \right)}_{CO} + N_2O \xrightarrow{H_2O} N_2 + OH^* + \underbrace{ \left(\begin{array}{c} N \\ N \end{array} \right)}_{CO} \underbrace{ \left(\begin{array}{c} CO \\ CO \end{array} \right)}_{CO} \end{array}$$
(1)





$$N_{2}O + 2e^{-} + \underbrace{\begin{pmatrix} CI \\ N \\ N \\ CO \end{pmatrix}}_{CO}^{CI} \xrightarrow{CI \\ CO \end{pmatrix}} N_{2} + OH^{-} + CI^{-} + \underbrace{\begin{pmatrix} N \\ N \\ N \\ CO \end{pmatrix}}_{CO}^{H} \xrightarrow{CO } (5)$$

The overall reaction at the level of the second CV wave thus corresponds to a net reduction of 0.5 N₂O per rhenium complex and a ligand exchange on the rhenium center (equation (5) in scheme 2b). Fast release of hydroxide requires a further reduction at more negative potential (third wave in figure 3a). This additional reduction regenerates the bi-reduced species $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ via a "Proton-Coupled Electron transfer"-type reaction ("PCET", *vide infra* in the discussion section) and catalysis can be sustained as summarized on scheme 3. This process parallels the required PCETs to release NH₃ from metal nitride complexes in nitrogen reduction reaction catalyzed by molecular catalysts. ⁶⁻¹¹

The established mechanism is at variance with the previously

suggested mechanism that was proposed on the sole basis of CV. ¹⁴ Our results show that formation of hydroxide as a byproduct of N₂O reduction is detrimental to catalysis because it is a strong coordinating ligand. Displacement of hydroxide is thus a requirement to get catalysis at lower overpotential. Moreover, the potential at which the initial reductive active species $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ is formed is related to the labile ligand X present on the initial complex $[\text{Re}(\text{bpy})(\text{CO})_3X]$. Therefore, we will now investigate the role of the labile ligand in the catalytic process.



Figure 3 [Re(bpy)(CO)₃Cl] 1 mM in CH₃CN + 0.1 M NBu₄PF₆ (a) CV at 0.1 V/s on a 3 mm-diameter GCE. under N₂O (black) and under argon (blue). Dashed line: direct reduction of N₂O in the absence of [Re(bpy)(CO)₃Cl] (b) Same as (a); the red CV is the second part of the black curve obtained by reversing the reverse scan at -1.25 V. (c) Linear scan voltammetry at 10 mV/s on a 5-mm diameter GC rotating disk electrode at 1000 rpm under N₂O. Vertical black arrows correspond to a stoichiometry of one electron per rhenium center.

Scheme 3. Catalytic reduction of N₂O via [Re^o(bpy^{•–})(CO)₃][–]



Behavior of $[Re(bpy)(CO)_3(CH_3CN)](PF_6)$ under N_2O

The reduction of [Re^I(bpy)(CO)₃(CH₃CN)]⁺ under argon shows an initial partially reversible one electron wave (standard potential -1.23 V) corresponding to the formation of $[Re^{I}(bpy^{-})(CO)_{3}(CH_{3}CN)]$ (wave 1/1' in figure 4a). Rapid loss of the labile acetonitrile ligand leads to partial formation of the [Re^o(bpy)(CO)₃]₂ dimer. A second wave corresponding to the formation of the bi-reduced species [Re^o(bpy^{•-})(CO)₃]⁻ is observed with a standard potential of -1.36 V (wave 2/2' in figure 4a) similar to what was previously reported for [Re(bpy)(CO)₃(Otf)]⁺ in THF 0.1 M NBu4PF6 THF electrolyte.²¹ The first and second reductions of the dimer occur at -1.52 V and -1.68 V respectively (waves 3/3' and 4/4' in figure 4a). Generation of the bi-reduced species $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^{-1}$ occurs at less negative potential than with [Re(bpy)(CO)₃Cl] (shift by ca. 300 mV) because decoordination of acetonitrile is easier than decoordination of chloride and also because the overall charge is neutral for the singly reduced solvato complex and anionic for the singly reduced chloro complex. When the solution is saturated with N₂O, important changes are observed on CV (Figure 4b). The first wave becomes almost irreversible and slightly increases in intensity. However it remains mono-electronic (Figure 4c) thus excluding a pathway via the bi-reduced species which formation requires an additional 100 mV overpotential. It is then followed by a reversible one-electron wave (Figure 4b) with a standard potential equal to -1.43 V. Finally a catalytic wave is obtained at the same position than the one obtained when starting from either $[\text{Re}^{I}(\text{bpy})(\text{CO})_{3}\text{Cl}]$ or $[\text{Re}^{I}(\text{bpy})(\text{CO})_{3}(\text{OH})]$ (Figure 4d). These observation strongly suggest that N₂O reacts with the mono-reduced species [Re^I(bpy•-)(CO)₃(CH₃CN)] (or presumably [Re^I(bpy⁻)(CO)₃]) on the timescale of CV. An exhaustive electrolysis of [Re(bpy)(CO)₃(CH₃CN)](PF₆) was thus performed at -1.22 V in the presence of a large excess of N₂O (see SI). The solution product was characterized by UVvis, IR and CV (Figure S4). It unambiguously shows that the

obtained product is $[Re^{1}(bpy)(CO)_{3}(OH)]$ which reduction corresponds to the reversible second wave observed on CV (Figure 4b). We also note that no dimer was formed during electrolysis (UV-vis) indicating that the reaction of N₂O with $[Re^{1}(bpy^{\bullet-})(CO)_{3}]$ is faster than dimerization.



Figure 4. CV in $CH_3CN + 0.1 M NBu_4PF_6$ at 0.1 V/s on a 3 mmdiameter GCE at 0.1 V/s. (a) [Re(bpy)(CO)₃(CH₃CN)](PF₆) 1 mM under argon (b) [Re(bpy)(CO)₃(CH₃CN)](PF₆) 1.6 mM under argon (blue) and under N₂O (red and black). (c) Linear scan voltammetry at 10 mV/s on a 5 mm-diameter GC rotat-1000 disk electrode at of ing rpm $[\text{Re(bpy)(CO)}_3(\text{CH}_3\text{CN})](\text{PF}_6)$ 1 mM in CH₃CN + 0.1 M NBu₄PF₆ under N₂O (black) and under argon (blue). Vertical black arrows correspond to a stoichiometry of one electron per rhenium center. (d) Normalized CV of $[Re(bpy)(CO)_3(CH_3CN)](PF_6)$ 1 mM under N₂O (blue), $[\text{Re(bpy)(CO)}_3\text{Cl}]$ 1 mМ under N_2O (black), $[\text{Re(bpy)(CO)}_3(\text{OH})]$ 1 mM under N₂O (red). i_n^0 is the peak current corresponding of a first one-electron wave of each catalyst under N₂O.

We have thus shown that reaction of N₂O with [Re^I(bpy⁺)(CO)₃] takes place on the timescale of CV at 0.1 V/s. Increasing the scan rate partially restores reversibility of the first CV wave (Figure S₅) indicating that the pseudo first order rate constant is of the order of $k_{ap}^{mono,ACN} \approx 10 \text{ s}^{-1}$ (see SI). It is smaller than the corresponding value for the reaction of [Re^o(bpy⁺⁻)(CO)₃]⁻ with N₂O (ca. 250 s⁻¹, *vide supra*). Importantly, the stoichiometry of the first wave remains one electron per rhenium center. This implies that the transformation of [Re^I(bpy)(CO)₃(CH₃CN)]⁺ to [Re^I(bpy)(CO)₃(OH)] is associated with the net reduction of 0.5 equivalent of N₂O and substitution of acetonitrile by hydroxide on the rhenium

center (scheme 4).

Scheme 4. Reduction of $[Re(bpy)(CO)_3(CH_3CN)]^+$ under N₂O.



Constant potential electrolysis was performed with continuous bubbling of N₂O at -1.22 V. UV-vis monitoring in the bulk shows the quantitative transformation of $[\text{Re}^{I}(\text{bpy})(\text{CO})_{3}(\text{CH}_{3}\text{CN})]^{+}$ to $[\text{Re}^{I}(\text{bpy})(\text{CO})_{3}(\text{OH})]$ (Figure 5a). The absorption at 450 nm, where only [Re^I(bpy)(CO)₃(OH)] absorbs, i.e. not at λ_{max} (see figures S6 for characteristics UV-vis spectrum of each species), varies at the same pace as the charge transferred at the electrode surface (Figure 5b). This confirms that the chemical transformation (equation 8 in scheme 4) following the electrochemical reduction of [Re^I(bpy)(CO)₃(CH₃CN)]⁺ (equation 7 in scheme 4) is fast. As sketched in figure 5c, it occurs in a diffusion reaction layer which thickness ($\mu \approx \sqrt{D/k_{ap}^{mono,ACN}} \approx 7 \,\mu\text{m}$ with $D \approx 5 \text{ 10}^{-6} \text{ cm}^2/\text{s}$ the rhenium complex diffusion coefficient and $k_{an}^{mono,ACN} \approx 10 \text{ s}^{-1}$ the pseudo-first order rate constant) is smaller than the diffusion layer (δ) set by the stirring of the solution probably in the order of tens of µm.²²



Figure 5. (a) Time evolution of UV-vis spectrum (1 scan / 250 s, l = 1 mm) of the bulk solution upon electrolysis at -1.22 V of [Re(bpy)(CO)₃(CH₃CN)](PF₆) 1 mM in CH₃CN + 0.1 M NBu₄PF₆ under N₂O. Blue: initial spectrum, red: final spectrum. (b) Full line: normalized absorption at 450 nm $x_A = A/A(t > 2000 \text{ s})$; dashed line: normalized charge consumed

 $x_Q = Q/nF$ where Q is the transferred charge and n is the ini-

tial quantity of moles of [Re(bpy)(CO)₃(CH₃CN)](PF₆). (c) Sketch of the spatial localization of the (electro)-chemical transformations during electrolysis.

Importantly, the oxidation state of the rhenium complex (Re(I)) is not modified at the end of the experiment. It means that the reaction can be potentially catalytic if the hydroxide ligand could be displaced. Since it is not possible when starting with $[Re^{I}(bpy)(CO)_{3}(CH_{3}CN)]^{+}$ because acetonitrile cannot displace hydroxide, we will now explore this possibility of a catalytic process when starting from $[Re^{I}(bpy)(CO)_{3}(CH)]$ and $[Re^{I}(bpy)(CO)_{3}(CI)]$.

Behavior of [Re(bpy)(CO)₃(OH)] and [Re(bpy)(CO)₃Cl] under N₂O upon monoelectronic reduction

On the timescale of CV (at 0.1 V/s), the mono-reduced complexes [Re¹(bpy^{•-})(CO)₃(OH)]⁻ and [Re¹(bpy^{•-})(CO)₃Cl]⁻ are stable both under argon and N₂O atmospheres as shown by the corresponding monoelectronic reversible waves (Figure S7). Under constant potential electrolysis conditions and stirring of the solution, the situation is different. At -1.52 V under argon, [Re(bpy)(CO)₃(OH)] is converted to [Re(bpy^{•-})(CO)₃(OH)]⁻ with a characteristic cell time constant $t_{cell} = \frac{V\delta}{SD} \approx 250$ s, where V is the cell volume, S the elec-

trode surface area, D the diffusion coefficient and δ the size of the diffusion layer set by the stirring of the solution (Figure S8). Under N₂O, a prolonged current is observed leading to the passage of 12 C after 4 h of electrolysis (Figure 6a), corresponding to 9.2 moles of electron per mole of rhenium complex in solution. UV-vis monitoring of the solution shows that [Re(bpy)(CO)₃(OH)] is slowly converted in the bulk (Figure 6b and SI). This indicates that, once formed at the electrode surface, $[Re^{I}(bpy^{\bullet-})(CO)_{3}(OH)]^{-}$ reacts with N₂O on its way to the bulk and [Re^I(bpy)(CO)₃(OH)] is regenerated. However, after ca 15 min (see figure S10), [Re¹(bpy)(CO)₃(OH)] starts to be converted in the bulk into a new compound with a broad absorption band in the visible (dark yellow spectrum in figure 6c). Such a band may suggest a decarbonylation of the rhenium complex ²³ but we cannot exclude formation of other "degraded" catalysts. The reactivity of $[\text{Re}^{I}(\text{bpy}^{\bullet-})(\text{CO})_{3}(\text{OH})]^{-}$ with N₂O was further confirmed via the electrogeneration of [Re^I(bpy^{•–})(CO)₃(OH)][–] under inert atmosphere by constant potential electrolysis of [Re^I(bpy)(CO)₃(OH)] at -1.52 V and then addition of a small excess of N₂O. As shown in figure S9, the time evolution of the UV-vis spectrum after addition of N₂O shows at 508 nm an initial fast decay that we attribute to the reaction of some bi-reduced species resulting from a slight overoxidation of [Re^I(bpy)(CO)₃(OH)] (see SI). Then a slow decay is observed corresponding to the reaction of [Re^I(bpy^{•-})(CO)₃(OH)]⁻ with N₂O. From this decay a rough evaluation of the pseudo first

order rate constant for the reaction of $[\text{Re}^{I}(\text{bpy}^{\bullet-})(\text{CO})_{3}(\text{OH})]^{-}$ with a saturated solution of N₂O is $k_{ap}^{mono,OH} = 0.04 \text{ s}^{-1}$. We thus conclude from these results that the electrochemical reduction of N2O is catalyzed by $[Re(bpy)(CO)_3(OH)]$ at a potential corresponding to the formation of the mono-reduced species but it is a slow process, probably limited by the unfavorable displacement of hydroxide by N₂O in [Re^I(bpy^{•-})(CO)₃(OH)]⁻. A concurrent decarbonylation of the catalyst may occur that is eventually detrimental to catalysis.



Figure 6. (a) Charge consumed upon electrolysis at -1.52 V of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$ 0.69 mM in 18 mL CH₃CN + 0.1 M NBu₄PF₆ under N₂O. (b) Time evolution of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$ concentration in the bulk solution calculated from the absorbance at 380 nm and 700 nm (see SI for details). (c) UV-vis of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$ 0.69 mM under N₂O before electrolysis (red) and after 4h electrolysis at -1.52V (dark yellow), l = 1 mm.

Starting from $[\text{Re}(\text{bpy})(\text{CO})_3\text{CI}]$, the process is more complex. Constant potential electrolysis at -1.42 V under argon shows the formation of $[\text{Re}(\text{bpy}^{\bullet-})(\text{CO})_3\text{CI}]^-$ together with the dimer $[\text{Re}^{\circ}(\text{bpy})(\text{CO})_3]_2$. Analysis of the time evolution of UV-vis spectra of the solution (see SI for details) indicates that $[\text{Re}(\text{bpy}^{\bullet-})(\text{CO})_3\text{CI}]^-$ initially builds up in the bulk of the solution and then decays at the expense of the dimer (Figure 7a). It is in line with a slow loss of chloride by $[\text{Re}(\text{bpy}^{\bullet-})(\text{CO})_3\text{CI}]^$ and the observation of a reversible monoelectronic CV wave for the reduction of $[\text{Re}(\text{bpy})(\text{CO})_3\text{CI}]$ at 0.1 V/s (Figure S7). The transformation of $[\text{Re}(\text{bpy})(\text{CO})_3\text{CI}]$ to the dimer $[\text{Re}(\text{bpy})(\text{CO})_3]_2$ is completed after 20 min and the consumption of 1.05 C corresponding to one electron per rhenium center. Under N₃O, application of a constant potential at -1.37 V leads to a prolonged current and the consumption of 3 C in 1.5 h (Figure 7b). The analysis of the time evolution of UV-vis spectra of the solution (see SI) shows that [Re(bpy)(CO)₃Cl] concentration only slowly decreases over time and that no dimer is formed as well as no intermediate [Re(bpy•-)(CO)₃Cl]-(Figure 7c). This again indicates that [Re(bpy•-)(CO)₃Cl]formed at the electrode surface at -1.37 V does not accumulate in the solution bulk but it reacts with N₂O with regeneration of [Re(bpy)(CO)₃Cl]. This reaction prevents evolution toward formation of the dimer seen under argon. The reaction is however slow enough for not taking place on the timescale of CV. Interestingly, we observe that, in the first 15 min, the decrease of [Re(bpy)(CO)₃Cl] concentration in solution is concomitant with the formation of [Re(bpy)(CO)₃(OH)] (red trace in figure 7c) and then the appearance of a new compound with a broad absorption band in the visible attributed to the non-identified "degraded" catalyst (Figure 7d) previously observed (figure 6c). Finally, electrolysis at -1.37 V performed in a tight cell under N2O atmosphere in the presence of [Re(bpy)(CO)₃Cl] as catalyst allows analysis of the gas in the headspace and reveals that after passing a charge of 10 C the faradaic yield for N_2O to N_2 conversion is 90% (see SI). These results support the homogeneous reduction of N₂O by the electrogenerated [Re(bpy⁻⁻)(CO)₃(Cl)]⁻ leading to hydroxide as co-product which accumulates in the solution and then progressively binds preferentially the rhenium center, slowing down catalysis and leading eventually to the degradation of the catalyst.



Figure 7. (a) Time evolution of $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ (black) and $[\text{Re}(\text{bpy}^-)(\text{CO})_3\text{Cl}]^-$ (green) and $[\text{Re}(\text{bpy})(\text{CO})_3]_2$ (magenta) concentrations in the bulk solution calculated from UV-vis absorbance (see SI for details) during electrolysis at -1.42 V of

 $[\text{Re}(\text{bpy})(\text{CO})_3\text{CI}]$ 1 mM in 11 mL CH₃CN + 0.1 M NBu₄PF₆ under argon. (b) Charge consumed upon electrolysis at -1.37 V of $[\text{Re}(\text{bpy})(\text{CO})_3\text{CI}]$ 0.83 mM in 18 mL CH₃CN + 0.1 M NBu₄PF₆ under N₂O. (c) Time evolution of $[\text{Re}(\text{bpy})(\text{CO})_3\text{CI}]$ (black) and $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$ (red) concentrations in the bulk solution calculated from UV-vis absorbance (see SI for details) at -1.37 V of $[\text{Re}(\text{bpy})(\text{CO})_3\text{CI}]$ 0.83 mM in 18 mL CH₃CN + 0.1 M NBu₄PF₆ under N₂O. Dark yellow: "degraded" catalyst (d) UV-vis spectrum of $[\text{Re}(\text{bpy})(\text{CO})_3\text{CI}]$ before electrolysis (black) and after 70 min electrolysis at -1.37 V under N₂O (dark yellow).

Direct evaluation of the pseudo-first order rate constant $k_{ap}^{mono,Cl}$ for reaction of $[\text{Re}(\text{bpy}^{\bullet-})(\text{CO})_3\text{Cl}]^-$ with N₂O is not possible because the reaction is too slow to take place on the CV timescale and the lifetime of $[\text{Re}^1(\text{bpy}^{\bullet-})(\text{CO})_3\text{Cl}]^-$ is too small to prepare it as a bulk solution by electrolysis and then add N₂O. However a lower limit of $k_{ap}^{mono,Cl}$ can be estimated from the absence of observation of $[\text{Re}(\text{bpy}^{\bullet-})(\text{CO})_3\text{Cl}]^-$ in the bulk under N₂O (Figure 7c). We obtain $k_{ap}^{mono,Cl} > 0.5 \text{ s}^{-1}$ (see SI for details).

From the observation that catalytic reduction of N₂O by the monoelectronic reduction of [Re(bpy)(CO)₃Cl] fades due to the chloride decoordination (equation (3)) and hydroxide coordination (equation (1)), we surmise that addition of an excess of free chlorides in the solution might allow sustaining catalysis by preventing hydroxide coordination to the rhenium center and/or displace hydroxide. Constant potential electrolysis at -1.37 V of a [Re(bpy)(CO)₃Cl] under N₂O atmosphere in the presence of 100 mM NEt₄Cl gives similar results as in the absence of NEt₄Cl but with higher current (Figure 8a). Unfortunately, after a while [Re(bpy)(CO)₃(OH)] accumulates in the solution, presumably because the concentration of hydroxide built from N₂O to N₂ conversion is high enough to prevent regeneration of [Re(bpy)(CO)₃Cl] (Figure 8b). At the same time, we again observe apparition of a new compound with a broad absorption band in the visible, the "degraded" catalyst, tentatively attributed to a decarbonylation product (Figure 8c).²³ Nonetheless, it appears that the presence of free chloride in large concentration in the solution boosts the initial reduction of N₂O.





Figure 8. (a) Charge consumed upon electrolysis at -1.37 V of $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ o.88 mM in 18 mL CH₃CN + o.1 M NBu₄PF₆ under N₂O with 100 mM NEt₄Cl. (b) Time evolution of $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ (black) and $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$ (red) concentrations in the bulk solution calculated from UV-vis absorbance (see SI for details) at -1.37 V of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{Cl})]$ o.88 mM in 18 mL CH₃CN + o.1 M NBu₄PF₆ under N₂O with 100 mM NEt₄Cl. Dark yellow: degradation product. (c) UV-vis spectrum of $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ before electrolysis (black) and after 120 min electrolysis at -1.37 V under N₂O (dashed red/dark yellow) with 100 mM NEt₄Cl.

Discussion

We have first shown that fast catalysis of N₂O electroreduction by $[Re(bpy)(CO)_3X]^{n+}$ complexes involves the formation of a bi-reduced species [Re^o(bpy^{•-})(CO)₃]⁻ as homogeneous reductant. A lower limit of the evaluated pseudo-first order rate constant in the presence of excess of N₂O (saturated in acetonitrile) and no specific addition of a proton donor, is $k_{ap}^{bi} = 250 \text{ s}^{-1}$ (step (1) in scheme 2). The corresponding expected catalytic plateau current in cyclic voltammetry considering pure kinetics conditions and scheme 3 as a mechanism is given by $i_{pl} = FS \sqrt{2Dk_{ap}^{bi}} = 337 \,\mu\text{A}$ that is of the order of magnitude of the catalytic current observed experimentally (Figure 3a). This indicates that the homogeneous reduction of N₂O by electrogenerated [Re^o(bpy^{•-})(CO)₃]⁻ is rate determining. However, as previously shown and recalled in figure S13, addition of water has two effects on the catalytic wave: (i) cathodic shift of the onset of the catalytic current noting that the shallow increase of the current is indicative of partial limitation by an electron transfer process and (ii) increase of the plateau current. In the framework of the established mechanism corresponding to scheme 3, these experimental features confirm that: (i) the reduction of [Re^I(bpy^{•-})(CO)₃(OH)]⁻ to the homogeneous reductive generate species $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ involves water and thus corresponds to a "PCET"-type process (scheme 3) and (ii) the chemical step of the fastest catalytic process involves a proton donor such as water. Hence, this excludes that the chemical reduction of N_2O by $[Re^o(bpy^{\bullet-})(CO)_3]^-$ is a simple outersphere electron transfer process. Moreover, if it were a simple outersphere electron transfer process the dimer [Re^o(bpy)(CO)₃]₂ would be formed from $[\text{Re}^{I}(\text{bpy}^{\bullet-})(\text{CO})_{3}]$. That it is not the case is attested by the final UV-vis spectrum showing no absorption at 590 and 780 nm (Figure 1a). Finally, based on the activation-driving force relationship previously uncovered for homogeneous outersphere reduction of $N_2O_1^{18}$ the evaluated rate constant $k_{ap}^{bi} = 250 \text{ s}^{-1}$ would correspond to an electron donor with a standard potential of ca. -1.97 V (Figure 9), i.e. much more negative than the oxidation potential of $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ evaluated above to be ca. -1.36 V (Figure 4a).



Figure 9. Rate constants (in s⁻¹) as function of the standard potential of the reductant E° (in V vs. SCE) for the homogeneous catalysis of reduction of N₂O. Blue data: reduction by electrogenerated anion radicals or dianions (from reference 18). The blue line corresponds to the prediction for outersphere electron transfers (see reference 18). Reduction by: $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ (black star), $[\text{Re}^1(\text{bpy}^{\bullet-})(\text{CO})_3]$ (black triangle), $[\text{Re}^1(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$ (black diamond), $[\text{Re}^1(\text{bpy}^{\bullet-})(\text{CO})_3\text{CI}]^-$ (black square). Partially adapted with permission from reference 18. Copyright 2021 RSC.

Our results confirm the innersphere character of the activation of N_2O by $[Re^o(bpy^{\bullet-})(CO)_3]^-$ in line with the requirement for the displacement of hydroxide from the pre-catalyst to trigger catalysis. It appears that water plays a crucial role in both the displacement of hydroxide (via the "PCET"-type step, equation (6)) and in the innersphere activation of the N-O bond (equation (1)). That the product formed from innersphere activation of N_2O by $[Re^o(bpy^{\bullet-})(CO)_3]^-$ is the hydroxide complex confirms the suggestion that N_2O binds the rhenium center via the oxygen atom and not the central electrophilic nitrogen. ²⁴ It is in line with the report that rhenium bipyridyl tri-carbonyl complexes are efficient photocatalysts for pyridine N-oxide deoxygenation. ¹⁷

We have then revealed that reaching the bi-reduced species $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ is not mandatory to activate and reduce $N_2\text{O}$. We have indeed shown that $[\text{Re}^{1}(\text{bpy}^{\bullet-})(\text{CO})_3]$ reduces $N_2\text{O}$ albeit with a slower rate than $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$, $k_{ap}^{mono,ACN} \approx 10 \text{ s}^{-1}$ (pseudo-first order rate constant in $N_2\text{O}$ saturated acetonitrile). Given the reductive power of $[\text{Re}^{1}(\text{bpy}^{\bullet-})(\text{CO})_3]$, corresponding to a standard potential of -1.23 V (Figure 4a), we can conclude that the reduction of $N_2\text{O}$ by $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]$ is an innersphere process because it is much faster than predicted for an outersphere electron transfer (Figure 9). Using $[\text{Re}^{1}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$ as a pre-catalyst was crucial as acetonitrile is a labile ligand allowing to

generate a vacant site on the rhenium center after a monoreduction of the complex. This contention is confirmed by our results showing that [Re^I(bpy^{•-})(CO)₃(OH)]⁻ is able to reduce N₂O (Figure 6) but with a small rate constant $k_{an}^{mono,OH}$ = 0.04 s-1 (pseudo-first order rate constant in N2O saturated acetonitrile). Taking into account the standard potential of $[Re(bpy)(CO)_3(OH)]^{\circ/-}$, -1.43 V, it appears that the rate constant $k_{ap}^{mono,OH}$ aligns on the activation-driving force correlation predicted for an outersphere electron transfer (Figure 9). Therefore, the strong ligand hydroxide, not able to be displaced by N₂O in [Re¹(bpy^{•-})(CO)₃(OH)]⁻, prevents an innersphere activation of N₂O. This confirms that an innersphere catalytic activation of N₂O requires the regeneration of a free coordination site on the rhenium and the formation of the strong ligand hydroxide as a co-product of N₂O reduction induces a self-inhibition of the catalysis. We have also shown that electrogeneration of [Re^I(bpy^{•-})(CO)₃Cl]⁻ allows reducing N₂O (Figure 7b) with a pseudo-first order rate constant $k_{ap}^{mono,Cl} > 0.5 \text{ s}^{-1}$. This rate constant does not correspond to a single event because it involves loss of chloride and reaction with N₂O. Knowing that the standard potential of $[\text{Re(bpy)(CO)}_3\text{Cl}]^{0/-}$ is -1.38 V, this lower limit of the rate constant indicates that the reaction is an innersphere process and not an outersphere electron transfer from $[\text{Re}^{I}(\text{bpy}^{\bullet-})(\text{CO})_{3}\text{Cl}]^{-}$ to N₂O (Figure 9). This indicates that chloride can be displaced by N₂O once the complex is monoreduced whereas hydroxide cannot be displaced by N₂O. It is in line with chloride being more labile than hydroxide as $[\text{Re}^{I}(\text{bpy}^{\bullet})(\text{CO})_{3}(\text{OH})]^{-}$ is stable in solution (Figure S8) whereas [Re^I(bpy^{•-})(CO)₃Cl]⁻ evolves toward formation of a dimer [Re(bpy)(CO)₃]₂ (Figure 7a). Interestingly, we have finally shown that, in the presence of large quantity of free chloride in solution, [Re^I(bpy•-)(CO)₃(OH)]⁻ can be converted back to [Re^I(bpy^{•-})(CO)₃Cl]⁻ via displacement of hydroxide by the free chloride, provided that the concentration of free hydroxide produced by the reduction of N₂O is not too 25 8). The exchange large (Figure OH-/Cl [Re^I(bpy^{•-})(CO)₃Cl]⁻ is confirmed by addition of excess of chlorides electrogenerated to an solution of $[\text{Re}^{I}(\text{bpy}^{\bullet-})(\text{CO})_{3}(\text{OH})]^{-}$ showing first formation of $[Re^{I}(bpy^{\bullet-})(CO)_{3}CI]^{-}$ and then evolution toward formation of the dimer $[Re(bpy)(CO)_3]_2$ (figure S15). Therefore the catalysis of N₂O reduction via an innersphere process induced by the mono-reduction of $[Re^{I}(bpy)(CO)_{3}(CI)]$ can be prolonged before switching to a slower outersphere process due to the formation of [Re(bpy)(CO)₃(OH)]. It is revealed by the time evolution of the charge which is initially fast (innersphere process) and then keeps increasing at a slower pace (outersphere process) when [Re(bpy)(CO)₃(OH)] is dominant in the bulk after 30 min electrolysis as seen in Figure 8. This illustrates the role of ligand exchange on the catalysts in the modulation of the rate of catalysis.

Scheme 5. General mechanism for the reduction of N_2O by $[Re(bpy)(CO)_3(X)]^{n+}$ complexes.



Based on all the results gathered in the present study, the general mechanism for N₂O electroreduction catalyzed by $[Re(bpy)(CO)_3(X)]^{n+}$ complexes (X = CH₃CN, Cl⁻, n = 0 or 1) can be summarized in scheme 5.

Conclusion

The electrochemical reduction of N₂O to N₂ is catalyzed by rhenium bipyridyl triscarbonyl complexes [Re(bpy)(CO)₂X]ⁿ⁺ $(X = CH_3CN, Cl^{-})$. A requirement for efficient catalysis is that the bi-reduced $[\text{Re}^{\circ}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ species is electrogenerated. However, the reaction generates hydroxide, a strong ligand making the potential needed to regenerate [Re^o(bpy^{•-})(CO)₃]⁻ more negative as the reaction progresses, amounting to a selfinhibition process. If the requirement is not fulfilled, a less efficient reduction is nonetheless taking place when monoreduced species $[\operatorname{Re}^{l}(bpy^{\bullet-})(CO)_{3}(X)]^{(n-1)+}$ are electrogenerated. An innersphere reduction of N₂O is triggered due to the lability of both acetonitrile and chloride allowing creating a free coordination site for N₂O binding. However, as in the case of the bi-reduced species pathway, generation of hydroxide as co-product induces formation of а $[Re(bpy)(CO)_3(OH)].$ reduction leads Its to $[Re^{I}(bpy^{\bullet-})(CO)_{3}(OH)]^{-}$ which is only competent for a slower outersphere reduction of N₂O due to the lack of lability of hydroxide. This can be overcome if a large concentration of free chloride is present enabling to displace hydroxide. These results emphasize the critical role of ligand exchange in the modulation of the rate of catalysis. Self-modulation of catalysis by ligand exchange is a phenomenon likely to take place in many electrochemical reactions catalyzed by transition metal complexes, in particular in the context of small molecules activation. We think that this study will be an incentive to bring more attention to this phenomenon in the endeavor to understand efficiency of molecular catalysis.

SUPPORTING INFORMATION

Experimental details. Determination of N_2O solubility in acetonitrile. Synthesis and characterization of

 $[\text{Re(bpy)(CO)}_3(\text{OH})]$. UV-vis spectrum of the various species. Additional UV-vis and IR spectro-electrochemical data. Analysis of time evolution of UV-vis during electrolysis. Additional CVs. Evaluation of rate constants. UV-vis of $[\text{Re(bpy)(CO)}_3(\text{OH})]$ in the presence of free chloride. This information is available free of charge on the ACS Publications website.

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Notes

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