Mechanistic Study of the Activation and the Electrocatalytic Reduction of Hydrogen Peroxide by Cu-tmpa in Neutral Aqueous Solution

Michiel Langerman and Dennis G. H. Hetterscheid*
# Table of Contents

1 Electrochemical experimental data ................................................................. 2  
   1.1 Catalyst concentration dependence studies .................................................. 2  
   1.2 Catalytic oxidation at high H₂O₂ concentrations ........................................... 3  
   1.3 FOWA of the HPRR in deuterated and non-deuterated solutions ..................... 3  
   1.4 Stability of Cu-trmpa in H₂O₂ ..................................................................... 5  

2 References ......................................................................................................... 5
1 Electrochemical experimental data

1.1 Catalyst concentration dependence studies

To determine the peak catalytic current $i_{\text{cat}}$ at low Cu-tmpa concentrations, the GC working electrode was polished before every catalytic measurement using a Struers LaboPol-30 polishing machine, using 1.0 µm diamond and 0.04 µm silica suspension on polishing cloths (Dur-type) for 1 min each. This was followed by sonication for 10 to 15 minutes in Milli-Q purified water. A similar process was followed for the experiments in D$_2$O, as described in the Experimental section of the main text. A blank CV was measured in a separate electrochemical cell by the GC electrode in an Ar saturated (1 atm) solution after every electrode polish to determine the quality of the polish and the size of the double layer. Fresh solutions containing Cu-tmpa and 1.1 mM H$_2$O$_2$ were used for every incremental increase of catalyst concentration. The currents obtained from CV measurements in presence of Cu-tmpa were corrected using their corresponding blank measurement, giving the catalytic current without any contribution from the double layer of the GC electrode to the catalytic current of the HPRR by Cu-tmpa.

![Log-log plot of the $i_{\text{cat}}$ (in A) vs. the Cu-tmpa concentration (in M) to determine the linearity of the dependence of the HPPR on Cu-tmpa, in the presence of 1.1 mM H$_2$O$_2$. The slope of the fit is 1.05 ($R^2 = 0.96$).](image1)

**Figure S1.** Log-log plot of the $i_{\text{cat}}$ (in A) vs. the Cu-tmpa concentration (in M) to determine the linearity of the dependence of the HPPR on Cu-tmpa, in the presence of 1.1 mM H$_2$O$_2$. The slope of the fit is 1.05 ($R^2 = 0.96$).

![Background corrected catalytic current $i_{\text{cat}}$ as a function of Cu-tmpa concentration with 10 mM H$_2$O$_2$. Log-log plot of the same data. Log($k_{\text{obs}}$) of the reduction of H$_2$O$_2$ as a function of Cu-tmpa concentration with 10 mM H$_2$O$_2$. Log($k_{\text{obs}}$) as a function of catalyst concentration. Conditions: pH 7 PB ([PO$_4$] = 100 mM), 293 K, 100 mV s$^{-1}$ scan rate.](image2)

**Figure S2.** a) Background corrected catalytic current $i_{\text{cat}}$ as a function of Cu-tmpa concentration with 10 mM H$_2$O$_2$. b) Log-log plot of the same data. c) $k_{\text{obs}}$ of the reduction of H$_2$O$_2$ as a function of Cu-tmpa concentration with 10 mM H$_2$O$_2$. d) Log($k_{\text{obs}}$) as a function of catalyst concentration. Conditions: pH 7 PB ([PO$_4$] = 100 mM), 293 K, 100 mV s$^{-1}$ scan rate.
1.2 Catalytic oxidation at high H$_{2}$O$_{2}$ concentrations

Figure S3. a) Zoom of the observed oxidation during cyclic voltammetry measurements of the reduction of H$_2$O$_2$ in the presence of 0.3 mM Cu-tmpa for a range of H$_2$O$_2$ concentrations; 40 (solid black)/60/80/100 (dashed) mM. b) CVs of a GC electrode in electrolyte solutions containing 1.5 (solid black) to 500 (dashed) mM H$_2$O$_2$. Conditions: pH 7 PB ([PO$_4$] = 100 mM), 293 K, 100 mV s$^{-1}$ scan rate.

1.3 FOWA of the HPRR in deuterated and non-deuterated solutions

The foot of the wave analysis (FOWA) is a powerful tool that can provide information about the rate-limiting step following the reduction of the catalyst.$^{1-5}$ For the HPRR by Cu-tmpa under aqueous conditions the rate limiting step in the catalytic cycle involves a concerted protonation and O–O bond breaking step. Thus, for the purpose of the FOWA the current-potential approximation as derived by Savéant et al.$^{1-2}$ for an EC$'$ type catalytic mechanism can be used for the electrochemical kinetics calculation (Eq S1). All electron transfer steps are considered to occur at the electrode, and no homogeneous electron transfer takes place between species.

$$i_c = \frac{nFSC_0^{\text{cat}}D_{\text{cat}}^{k_{\text{obs}}}}{1 + \exp\left[\frac{F}{RT}(E - E_{1/2})\right]}$$  (S1)

Where $F$ is the faradaic constant, $S$ the surface area of the electrode, $C_0^{\text{cat}}$ the bulk catalyst concentration, $D_{\text{cat}}$ the diffusion coefficient of the catalyst, $E_{1/2}$ the equilibrium potential of the catalyst redox couple, and $k_{\text{obs}}$ the observed rate constant, with $k_{\text{obs}} = \text{TOF}_{\text{max}}$. Eq S1 can be normalized with the peak current of the one-electron reduction of the catalyst ($i_p$) using the Randles-Sevcik equation (Eq S2), resulting in Eq S3.

$$i_p = 0.446nFC_0^{\text{cat}}\sqrt{\frac{FD_{\text{cat}}}{RT}}$$  (S2)

$$\frac{i_c}{i_p} = \frac{2.24n_{\text{cat}}\sqrt{RT/FV}\text{TOF}_{\text{max}}}{1 + \exp\left[\frac{F}{RT}(E - E_{1/2})\right]}$$  (S3)

Where $n_{\text{cat}}$ is the number of electrons used in the catalytic cycle in the FOWA region, which is 2 electrons in the case of the reduction of H$_2$O$_2$ to water. As a plateau current is not reached, the analysis can only be applied at the foot of the catalytic wave, where no side-phenomena take place. We also note that the half-wave potential of the catalytic wave $E_{\text{cat}/2} > E_{1/2}$ in CV measurements in the presence of 0.3 mM Cu-tmpa, due to substrate depletion near the electrode. As $\exp[F/RT(E - E_{1/2})] \gg 1$ in the foot-of-the-wave potential window, Eq 6 can be simplified to Eq S4. Using Eq S4, TOF$_{\text{max}}$ can be derived from the slope of $i_c/i_p$ vs. $\exp[-F/RT(E - E_{1/2})]$.

$$\frac{i_c}{i_p} = 2.24n\sqrt{\frac{RT}{FV}\text{TOF}_{\text{max}}\exp[-F/RT(E - E_{1/2})]}$$  (S4)
Additionally, mechanistic insight can be obtained from FOW analysis. In case of a first order relationship in catalyst, the catalytic current should be linear with $1 + \exp\left[\frac{F}{RT} (E - E_{1/2})\right]$, while for a homolytic second order reaction the catalytic current should be linear with $\left(1 + \exp\left[\frac{F}{RT} (E - E_{1/2})\right]\right)^{3/2}$. When the current-potential relationship for a binuclear homolytic reaction were applied, very poor linearity was observed. Thus, plots of $i_c/i_p$ vs. $\exp\left[-\frac{F}{RT} (E - E_{1/2})\right]$ were fitted linearly between the onset of the ORR, here defined as $i_c/i_{\text{redox}} \geq 2$, and at which $i_c/i_p$ is at least larger than 1.6. Here, $i_{\text{redox}}$ is the current associated with the reduction of the catalyst measured at the applied potential $E$, in the absence of $\text{H}_2\text{O}_2$. Measurements were repeated three times and FOWA was performed on the individual measurements. Averaging of the results obtained for the individual experiments led to the TOF$_{\text{max}}$ as reported with the standard error.

Figure S4. Triplicate CVs of the reduction of 1.1 mM $\text{H}_2\text{O}_2$ in the presence of 0.3 mM Cu-tmpa in non-deuterated (a) and deuterated (b) PB electrolyte solutions under 1 atm Ar. FOWA of the HPRR for non-deuterated (c) and deuterated (d) conditions, where $f = F/RT$. Corresponding fits of the linear regions of the FOWA for non-deuterated (e) and deuterated (f) conditions, $R^2 \geq 0.98$. Conditions: pH 7 PB ([PO$_4$] = 100 mM), 293 K, 100 mV s$^{-1}$ scan rate.
1.4 Stability of Cu-tmpa in H$_2$O$_2$

Figure S5. a) CVs showing 25 consecutive scans of the catalytic reduction of H$_2$O$_2$ (10 mM) by Cu-tmpa (8.0 µM) under 1 atm Ar. A clear increase in catalytic current is observed with each scan, from the first scan (blue) to the last scan (red). b) CVs of the same solution after mixing and saturating the solution for 1 min with 1 atm Ar, while keeping the electrode submerged in the solution. A large initial catalytic current is observed as the H$_2$O$_2$ near the electrode has been replenished by mixing, indicating a deposition has formed on the electrode during the experiment shown in (a). Conditions: pH 7 PB ([PO$_4$]$^-$ = 100 mM), 293 K, 100 mV s$^{-1}$ scan rate.

2 References

[1] C. Costentin, S. Drouet, M. Robert, J.-M. Savéant, J. Am. Chem. Soc. 2012, 134, 11235-11242.
[2] C. Costentin, J.-M. Savéant, ChemElectroChem 2014, 1, 1226-1236.
[3] E. S. Rountree, B. D. McCarthy, T. T. Eisenhart, J. L. Dempsey, Inorg. Chem. 2014, 53, 9983-10002.
[4] V. Artero, J.-M. Saveant, Energy & Environmental Science 2014, 7, 3808-3814.
[5] C. Costentin, J.-M. Savéant, J. Am. Chem. Soc. 2017, 139, 8245-8250.