ELECTRONIC SUPPLEMENTARY INFORMATION

Collecting meaningful early-time kinetic data in homogeneous catalytic water oxidation with a sacrificial oxidant

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Derivation of equation 9:

From the text:

$$Ru^{3+} \xrightarrow{k_2} products \qquad (2)$$

In the presence of WOC four oxidative equivalents of Ru^{3+} are used to oxidize water in eq 3.

$$4\,Ru^{3+} + 2\,H_2O \xrightarrow{k_3} 4\,Ru^{2+} + O_2 + 4\,H^+ \qquad (3)$$

The simplified mechanism of catalytic water oxidation is given in eqs 4-8:

$$Ru^{3+} + cat(0) \xrightarrow{k_4} Ru^{2+} + cat(1) \qquad (4)$$

$$Ru^{3+} + cat(1) \xrightarrow{k_5} Ru^{2+} + cat(2) \qquad (5)$$

$$Ru^{3+} + cat(2) \xrightarrow{k_6} Ru^{2+} + cat(3) \qquad (6)$$

$$Ru^{3+} + cat(3) \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} Ru^{2+} + cat(4) \qquad (7)$$

$$cat(4) + 2\,H_2O \xrightarrow{k_8} cat(0) + O_2 + 4\,H^+ \qquad (8)$$

where “i” in cat(i) is the number of electrons removed from the resting oxidation state of a catalyst. The first three reactions are assumed to be fast and the [cat(0)], [cat(1)], [cat(2)], [cat(3)], [cat(4)] to be steady state. Under these assumptions and taking into account the mass balance for total catalyst concentration [cat] the rate law of Ru^{3+} consumption is in eq 9…

$$\frac{-d[Ru^{3+}]}{dt} = k_2[Ru^{3+}] + \frac{4k_8k_7[Ru^{3+}][cat]}{(k_7[Ru^{3+}] + k_{-7}[Ru^{2+}] + k_8)} \qquad (9)$$

Derivation of equation 9:

$$\frac{-d[Ru^{3+}]}{dt} = k_2[Ru^{3+}] + k_4[Ru^{3+}][cat(0)] + k_5[Ru^{3+}][cat(1)] + k_6[Ru^{3+}][cat(2)] + k_7[Ru^{3+}][cat(3)] - k_{-7}[Ru^{2+}][cat(4)]$$

(S1)

Steady state condition with respects to cat(i):

$$i = 1;\ k_4[cat(0)][Ru^{3+}] = k_5[cat(1)][Ru^{3+}] \quad (S2)$$

$$i = 2;\ k_5[cat(1)][Ru^{3+}] = k_6[cat(2)][Ru^{3+}] \quad (S3)$$

$$i = 3;\ k_6[cat(2)][Ru^{3+}] - k_7[cat(3)][Ru^{3+}] + k_{-7}[cat(4)][Ru^{2+}] = 0; \quad (S4)$$

$$i = 4;\ k_7[cat(3)][Ru^{3+}] - k_{-7}[cat(4)][Ru^{2+}] - k_8[cat(4)] = 0 \quad (S5)$$

From these eqs, we obtain:

$$k_8[cat(4)] = k_6[cat(2)][Ru^{3+}],\ k_6[cat(2)][Ru^{3+}] = k_5[cat(1)][Ru^{3+}] = k_4[cat(0)][Ru^{3+}] \quad (S6)$$

thus,

$$\frac{-d[Ru^{3+}]}{dt} = k_2[Ru^{3+}] + k_7[Ru^{3+}][cat(3)] - k_{-7}[Ru^{2+}][cat(4)] + 3k_8[Ru^{3+}][cat(4)]$$
(S7)

The mass balance with respect to the catalyst gives:

$$[cat(0)]\left(1 + \frac{k_4}{k_5} + \frac{k_5}{k_6}\right) + [cat(3)] + [cat(4)] = [cat] \quad (S8)$$

where

$$\frac{k_4}{k_5} \approx \frac{k_5}{k_6} \approx 1 \quad (S9)$$

Eq S6 can be re-arranged to:

$$[cat(0)] = [cat(4)]\left(\frac{k_8}{k_4[Ru^{3+}]}\right) \quad (S10)$$

If the reactions 4-6 are fast, or $k_8 << k_4[Ru^{3+}]$, then $[cat(4)] >> [cat(0)]$, $[cat(4)] >> [cat(1)]$, and $[cat(4)] >> [cat(2)]$. In this case the mass balance in eq S8 is simplified to:

$$[cat(3)] = [cat] - [cat(4)] \quad (S11)$$

Inserted into eq S4 from above gives:

$$k_7[cat(3)][Ru^{3+}] = k_{-7}[cat(4)][Ru^{2+}] + k_8[cat(4)] \quad (S12)$$

$$k_7([cat] - [cat(4)])[Ru^{3+}] = k_{-7}[cat(4)][Ru^{2+}] + k_8[cat(4)] \quad (S13)$$

$$[cat(4)] = \frac{k_7[Ru^{3+}][cat]}{(k_7[Ru^{3+}] + k_{-7}[Ru^{2+}] + k_8)}$$
(S14)

Inserting this into eq S1:

$$\frac{-d[Ru^{3+}]}{dt} = k_2[Ru^{3+}] + k_7[Ru^{3+}]([cat] - [cat(4)]) - k_{-7}[Ru^{2+}][cat(4)] + 3k_8[Ru^{3+}][cat(4)]$$
(S15)

$$\frac{-d[Ru^{3+}]}{dt} = k_2[Ru^{3+}] + k_7[Ru^{3+}][cat] - k_7[Ru^{3+}][cat(4)] - k_{-7}[Ru^{2+}][cat(4)] + 3k_8[Ru^{3+}][cat(4)]$$
(S16)

$$\frac{-d[Ru^{3+}]}{dt} = k_2[Ru^{3+}] + k_7[Ru^{3+}][cat] - k_7[Ru^{3+}]\left(\frac{k_7[Ru^{3+}][cat]}{(k_7[Ru^{3+}] + k_{-7}[Ru^{2+}] + k_8)}\right) - k_{-7}[Ru^{2+}]\left(\frac{k_7[Ru^{3+}][cat]}{(k_7[Ru^{3+}] + k_{-7}[Ru^{2+}] + k_8)}\right) + 3k_8[Ru^{3}$$

(S17)

Rearrangement of eq S17 produces eq S18 (which is eq 9 from the text):

$$\frac{-d[Ru^{3+}]}{dt} = k_2[Ru^{3+}] + \left(\frac{4k_8k_7[Ru^{3+}][cat]}{(k_7[Ru^{3+}] + k_{-7}[Ru^{2+}] + k_8)}\right)$$

(S18)