

ELECTRONIC SUPPLEMENTARY INFORMATION

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

James W. Vickers,^a Jordan M. Sumliner,^a Hongjin Lv,^a Mike Morris,^b Yurii V. Geletii,^{a*} and Craig L. Hill^{a*}

^a Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, GA 30322.

^b SpectrEcology, Jasper, GA, 30143, United States.

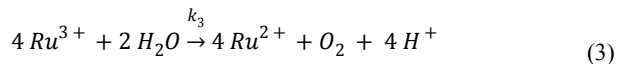
* Corresponding authors: chill@emory.edu and iguelet@emory.edu

Derivation of equation 9:

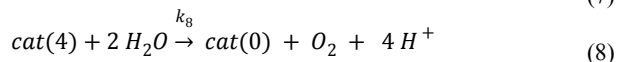
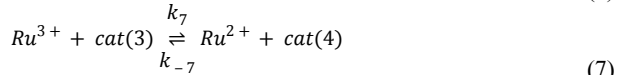
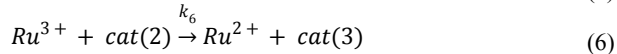
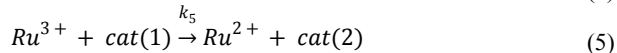
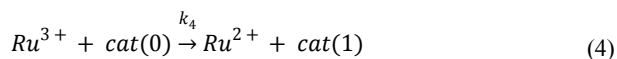
From the text:



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



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



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...

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

Derivation of equation 9:

$$\frac{-d[Ru^{3+}]}{dt} = k_2[Ru^{3+}] + k_4[Ru^{3+}][cat(0)] + k_5[Ru^{3+}][cat(1)] + k_6[Ru^{3+}][cat(2)] + k_7[Ru^{3+}][cat(3)] - k_{-7}[Ru^{2+}][cat(4)] \quad (S1)$$

Steady state condition with respects to cat(i):

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

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

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

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

From these eqs, we obtain:

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

thus,

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

The mass balance with respect to the catalyst gives:

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

where

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

Eq S6 can be re-arranged to:

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

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

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

Inserted into eq S4 from above gives:

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

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

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

Inserting this into eq S1:

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

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

$$\frac{-d[\text{Ru}^{3+}]}{dt} = k_2[\text{Ru}^{3+}] + k_7[\text{Ru}^{3+}][\text{cat}] - k_7[\text{Ru}^{3+}] \left(\frac{k_7[\text{Ru}^{3+}][\text{cat}]}{(k_7[\text{Ru}^{3+}] + k_{-7}[\text{Ru}^{2+}] + k_8)} \right) - k_{-7}[\text{Ru}^{2+}] \left(\frac{k_7[\text{Ru}^{3+}][\text{cat}]}{(k_7[\text{Ru}^{3+}] + k_{-7}[\text{Ru}^{2+}] + k_8)} \right) + 3k_8[\text{Ru}^{3+}] \left(\frac{k_7[\text{Ru}^{3+}][\text{cat}]}{(k_7[\text{Ru}^{3+}] + k_{-7}[\text{Ru}^{2+}] + k_8)} \right) \quad (\text{S17})$$

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)