

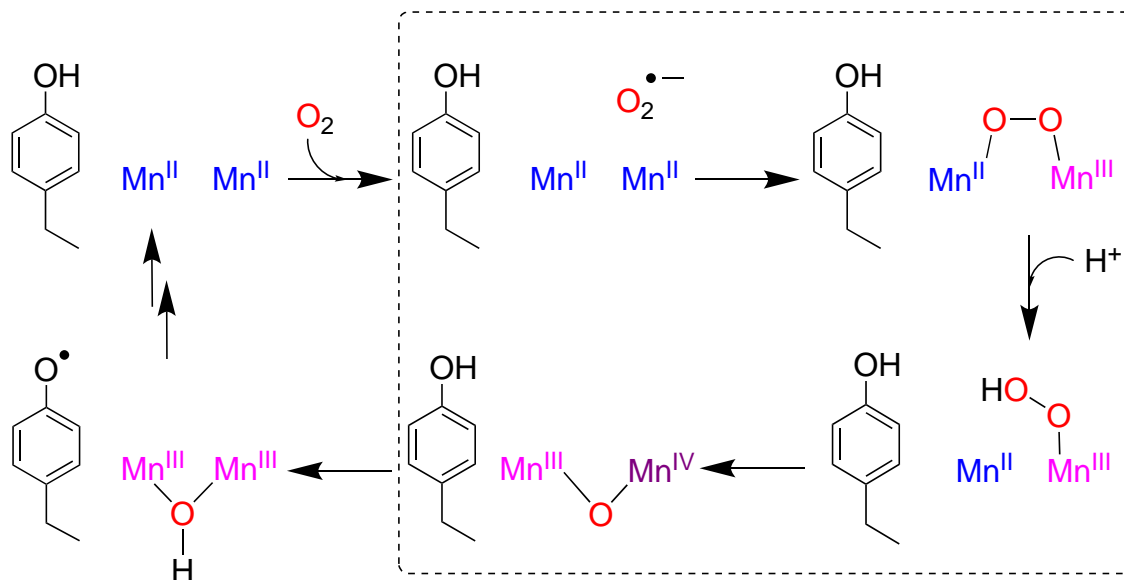
## Mimicking class Ib dimanganese ribonucleotide reductase

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A fascinating facet of ribonucleotide reductase's (RNRs) Chemistry has been the identification of a dimanganese ( $Mn_2$ ) active site in class Ib RNRs that requires superoxide anion ( $O_2^{\bullet-}$ ), rather than dioxygen ( $O_2$ ), to access a high-valent  $Mn^{III}Mn^{IV}$  oxidant via a  $Mn^{II}Mn^{III}$ -peroxide precursor (see scheme). We have prepared two  $Mn^{II}_2$  complexes that, upon exposure to  $KO_2$ , yield  $Mn^{II}Mn^{III}$ -peroxide adducts. Activation of the  $Mn^{II}Mn^{III}$ -peroxide complexes either via thermal decay or acid-activation results in meta-stable  $Mn^{III}Mn^{IV}$  adducts. The  $Mn^{II}Mn^{III}$ -peroxide complexes displayed electronic absorption features typical of a Mn-peroxide species, and either a 29- or 22-line EPR signal typical of a  $Mn^{II}Mn^{III}$  entity. The  $Mn^{III}Mn^{IV}$  adducts displayed electronic absorption features typical of a  $Mn^{III}Mn^{IV}$  species, and 16-line EPR signal typical of a  $Mn^{III}Mn^{IV}$  entity. Electrospray ionisation mass spectrometry (ESI-MS) confirmed the elemental composition of the  $Mn^{II}Mn^{III}$ -peroxides and  $Mn^{III}Mn^{IV}$  complexes. While the  $Mn^{II}Mn^{III}$ -peroxides were unreactive towards weak O–H bonds (as those found in tyrosine), the  $Mn^{III}Mn^{IV}$  complexes were found to be efficient oxidants, capable of phenol O–H bond activation via rate limiting electron transfer. Our findings provide comprehensive support for the postulated mechanism of  $O_2$  activation at class Ib  $Mn_2$  RNRs.



### References:

- [1] Adriana M. Magherusan, Ang Zhou, Erik R. Farquhar, Max García-Melchor, Brendan Twamley, Lawrence Que, Jr., Aidan R. McDonald, *Angew. Chem. Int. Ed.* **2018** 57, 918-922.  
 [2] Adriana M. Magherusan, Subhasree Kal, Daniel N. Nelis, Lorna M. Doyle, Erik R. Farquhar, Lawrence Que, Jr., Aidan R. McDonald *Angew. Chem. Int. Ed.* **2019**, DOI:10.1002/anie.201900717R1