Illuminating Mechanisms of Water Oxidation Catalysis 50046-ND3

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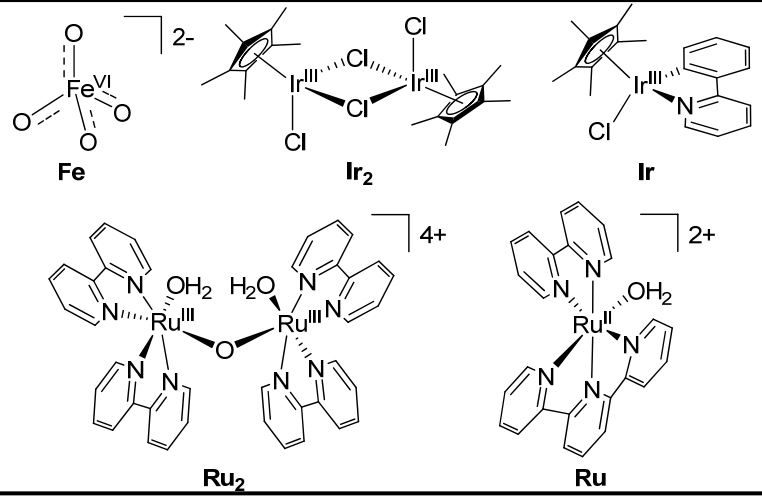
Natural abundance oxygen kinetic isotope effects are being measured and calculated using DFT to probe mechanisms of water oxidation.



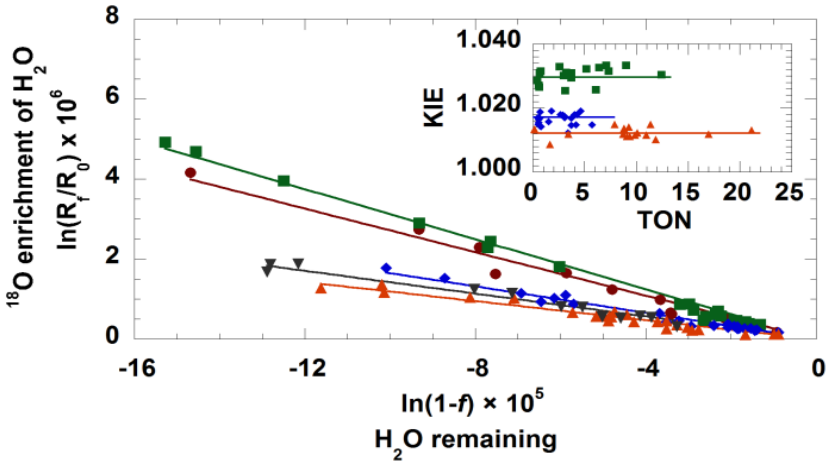
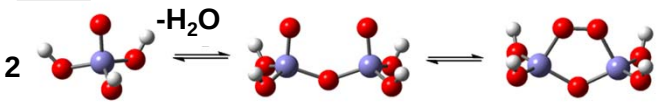


Figure (top right): Isotope fractionation of H_2O determined from $^{18}O/^{16}O$ of O_2 evolved by **Fe** (red circles), **Ru** (green squares), **Ru$_2$** (blue diamonds), **Ir** (inverted black triangles) and **Ir$_2$ (**orange triangles) in presence of CAN. Inset: ^{18}O KIEs at variable turnover numbers (TONs).

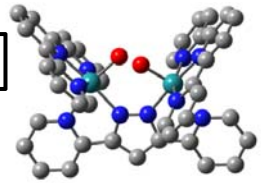
Radical coupling (RC) transition states:

Fe



^{18}O KIE$_{exp}$ = 1.0280 **^{18}O KIE$_{calc}$ = 1.0311**

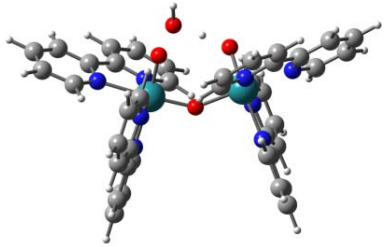
Ru$_2$hbpp



^{18}O KIE$_{exp}$ = 1.0355
^{18}O KIE$_{calc}$ = 1.0430

Radical attack (RA) transition state:

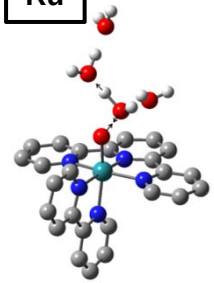
Ru$_2$ (“blue dimer”)



^{18}O KIE$_{exp}$ = 1.0168
^{18}O KIE$_{calc}$ = 1.0146

Nucleophilic attack (NA) transition state:

Ru



^{18}O KIE$_{exp}$ = 1.0327
^{18}O KIE$_{calc}$ = 1.0322

Ir

^{18}O KIE$_{exp}$ = 1.0140
^{18}O KIE$_{calc}$ = 1.0102