REACTIVITY OF THE FIRST CHARACTERIZED HIGH-VALENT METAL-OXO SPECIES

PIRINEUS

Led by

M. SWART

Leader (PI)

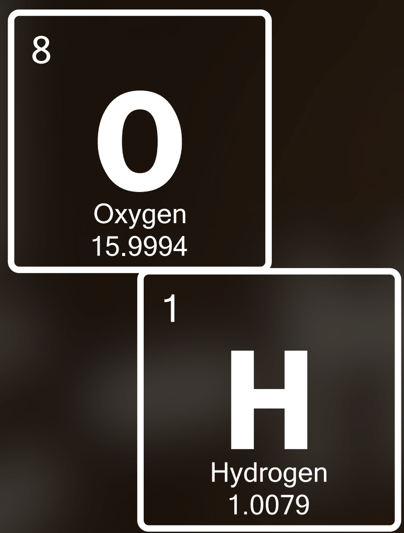
Universitat de Girona

F. AHSAN

PhD student

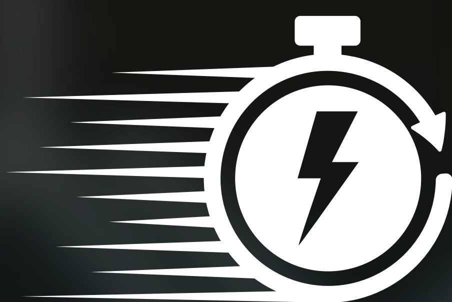
Universitat de Girona

1 METAL-BASED MOLECULES: POWERFUL BUT HARD TO STUDY



Many chemical reactions in nature and industry are **driven by metal-based molecules** that transfer oxygen or hydrogen atoms

Some versions of these molecules **react much faster than others**, but they are difficult to study experimentally



Understanding why this happens is a **key step to design better catalysts**

A FUNDAMENTAL DILEMMA IN CHEMISTRY 2

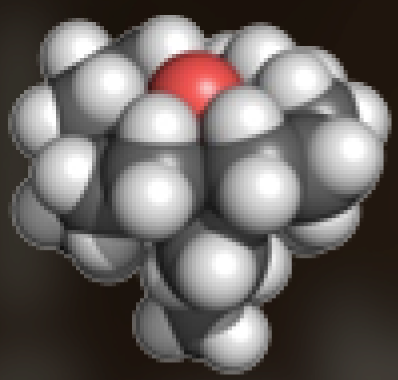
Chemists use **spectroscopy techniques** to study the structure and behaviour of reactive molecules

However, the more reactive the molecule, **the harder it is to capture its behaviour**

This results in a dilemma: **we want to have reactive species,** but we also want to be able to characterize them with spectroscopy

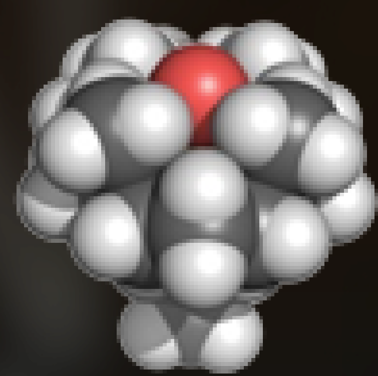
We cannot have both at the same time

3 TWO SIMILAR MOLECULES, ONE BIG DIFFERENCE



In 2003, they obtained **the crystal structure of a high-valent molecule with an iron-oxygen core** for the first time

In 2015, they synthesized a new version with the reactive group **on the same side as the neighbouring methyls**



The two versions **result from different processes**: the 1st forms by reaching equilibrium slowly, the 2nd is intentionally interrupted early

But their reactivities greatly differ: one reacts **up to 1000 times faster in oxygen transfer,** and the reason wasn't clear

THE ROLE OF **HPC RESOURCES**

4

Computational chemistry can, in principle, **determine everything in this reaction**, if given enough parameters

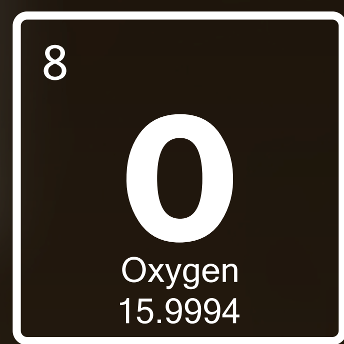
Modelling **the energy states of these molecules** correctly and accurately is challenging, and requires massive resources

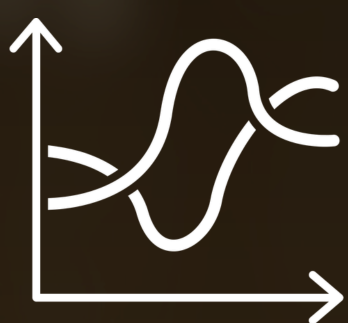
Thanks to RES resources, **they could map all reaction pathways and energy surfaces** for different spin states for multiple versions of the molecule

5 THE SOLVENT THAT SOLVES THE PUZZLE

The team found that **subtle changes in the faster molecule's electronic structure** made it slightly more reactive (2-3 times) in hydrogen transfer

But the 1000 factor in oxygen transfer comes from another process: **a solvent molecule (acetonitrile) that detaches during the reaction**





This process **lowers the energy barrier** of the acceptor orbital and accelerates the reaction

In the other molecule, **weak interactions** between the solvent and **the methyls near the reactive group** prevent it

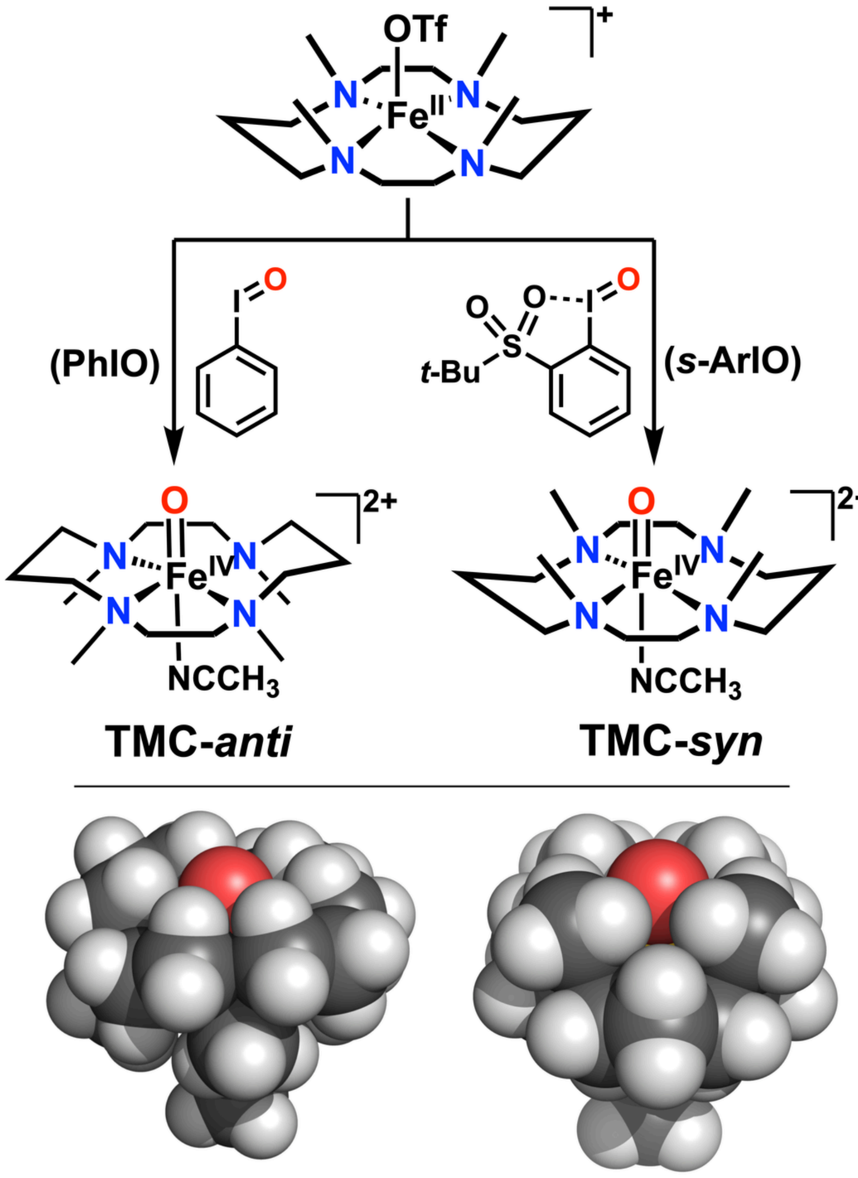


Figure 1.
Synthetic routes to TMC-*anti* (2003 molecule) and TMC-*syn* (2015 molecule) Fe(IV)=O complexes.

(Reproduced with permission from Proc. Natl. Acad. Sci. USA 2024, 121, e2319799121)

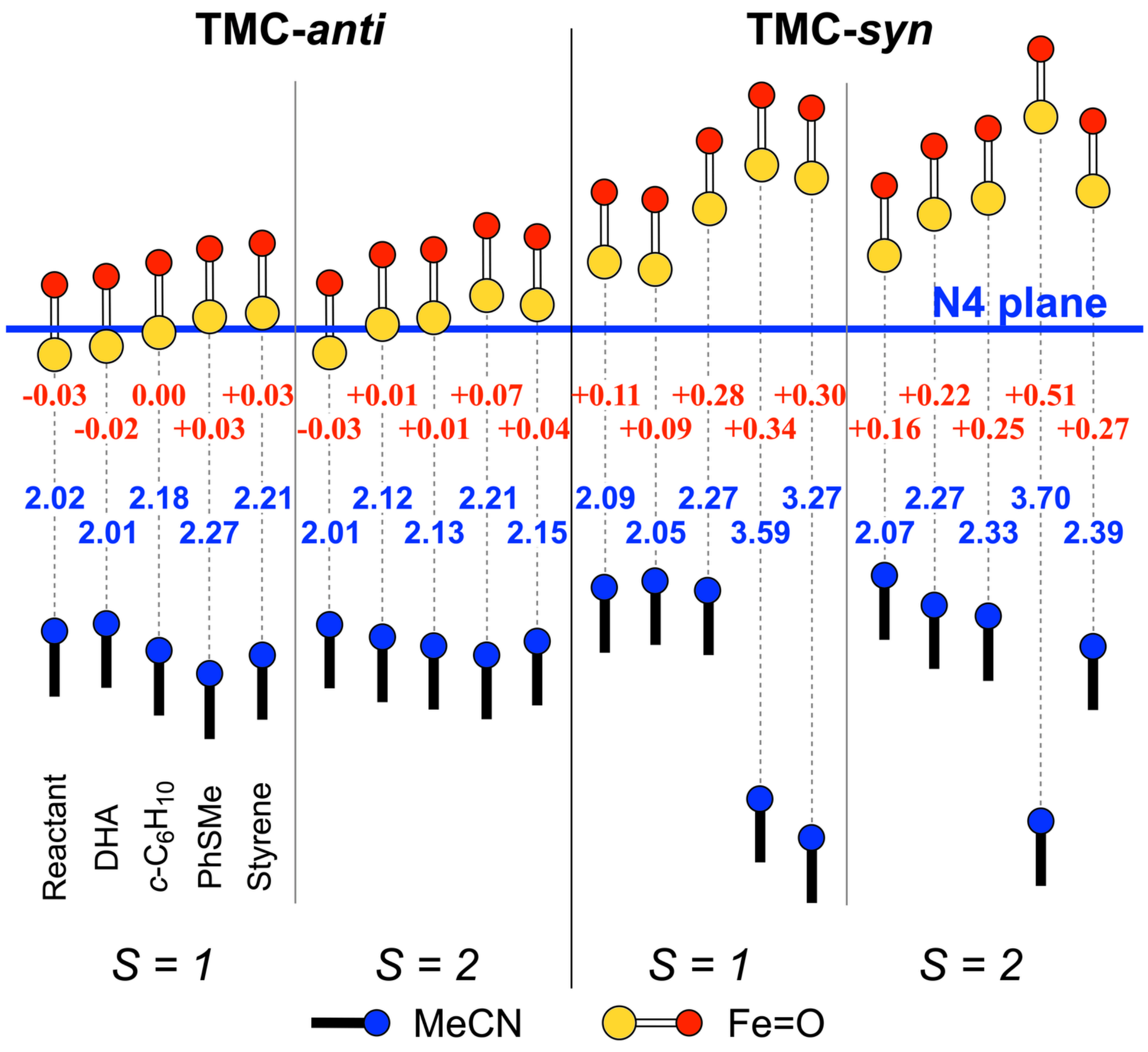


Figure 2.
Positions of the Fe-O core and the solvent molecule relative to the molecular plane, for both versions of the molecule and different reaction types. The dotted lines show the distance between the iron atom and the solvent.

(Reproduced with permission from Proc. Natl. Acad. Sci. USA 2024, 121, e2319799121)

ICTS
INFRAESTRUCTURAS CIENTÍFICAS Y TÉCNICAS SINGULARES
EuroCC SPAIN RES
BSC Barcelona Supercomputing Center
Centro Nacional de Supercomputación
ICREA
Universitat de Girona