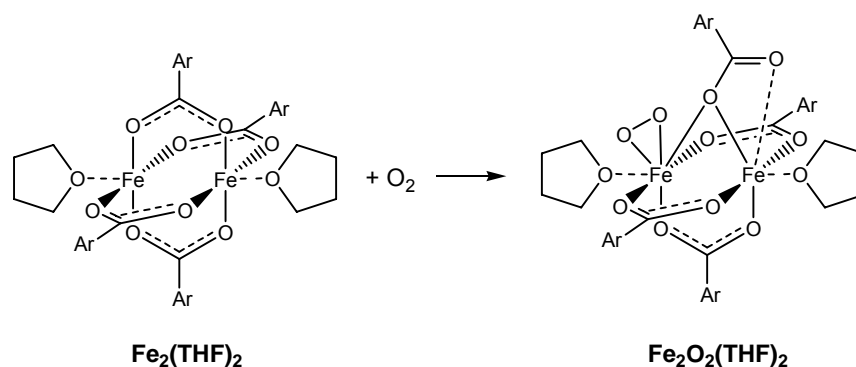


Workshop 6

The Tolman and Que groups have investigated the reactivity of (peroxo)diiron compounds as oxidative intermediates, with the goal of understanding biological iron complexes with similar structures that use molecular oxygen as an oxidant. For example, the peroxo complex labeled " $\text{Fe}_2\text{O}_2(\text{THF})_2$ " below can be prepared by exposing $\text{Fe}_2(\text{THF})_2$ to oxygen.¹



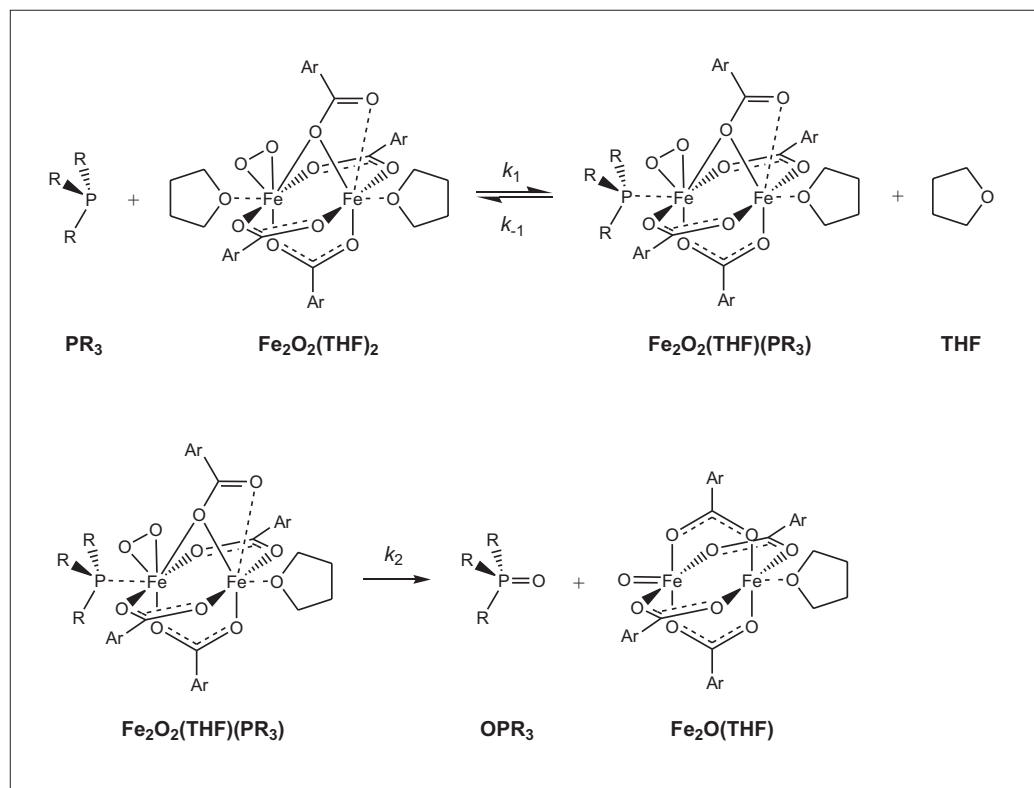
$\text{Fe}_2\text{O}_2(\text{THF})_2$ can then be used to oxidize substrates; for example, $\text{Fe}_2\text{O}_2(\text{THF})_2$ converts phosphines (PR_3) to phosphine oxides (OPR_3). Kinetic evidence indicated that the oxidation step involved coordination of the phosphine to the diiron species, and that as a result a THF ligand might make way for the phosphine via displacement (Mechanism 1, next page) or dissociation (Mechanism 2). Tolman and Que attempted to determine which of these mechanisms better describes this process. In their study, rate data was collected as pseudo-first order decays of $\text{Fe}_2\text{O}_2(\text{THF})_2$, where

$$\frac{\partial[\text{Fe}_2\text{O}_2(\text{THF})_2]}{\partial t} = -k_{\text{obs}}[\text{Fe}_2\text{O}_2(\text{THF})_2].$$

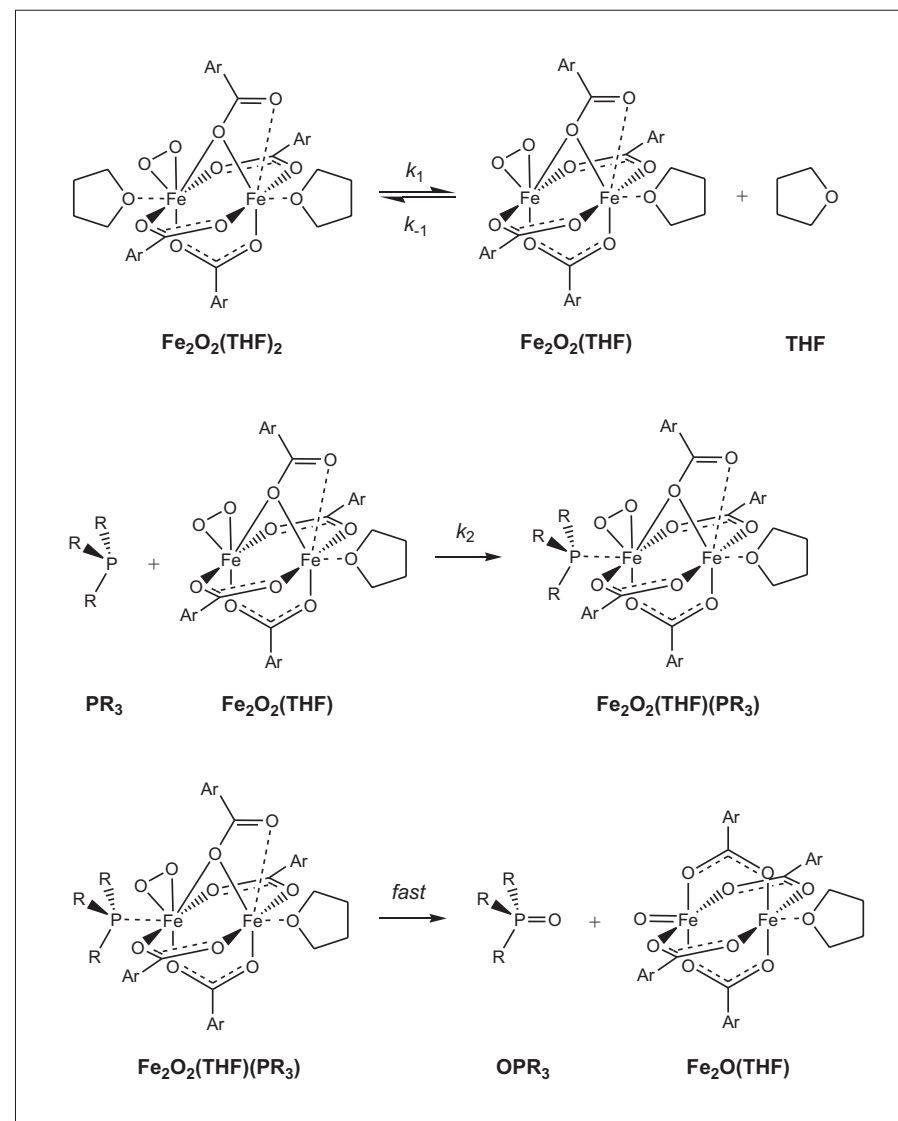
- a. Using the steady-state assumption, write rate laws for $\partial[\text{Fe}_2\text{O}_2(\text{THF})_2]/\partial t$ in the form of the expression above for each of the two mechanisms on the next page. How is k_{obs} defined in each case?

¹ Kryatov, S. V.; Chavez, F. A.; Reynolds, A. M.; Rybak-Akimova, E. V.; Que, L., Jr.; Tolman, W. B. *Inorg. Chem.* **2004**, *43*, 2141-2150.

Mechanism 1
(Associative)



Mechanism 2
(Dissociative)

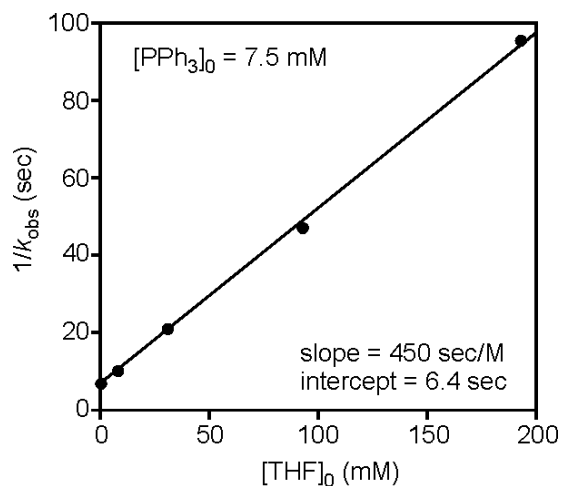
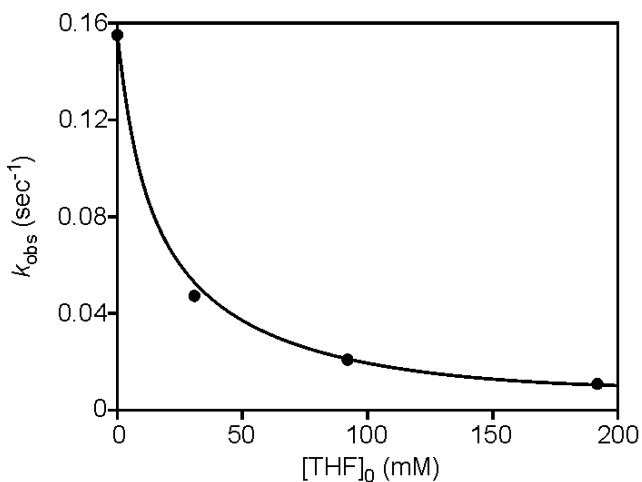
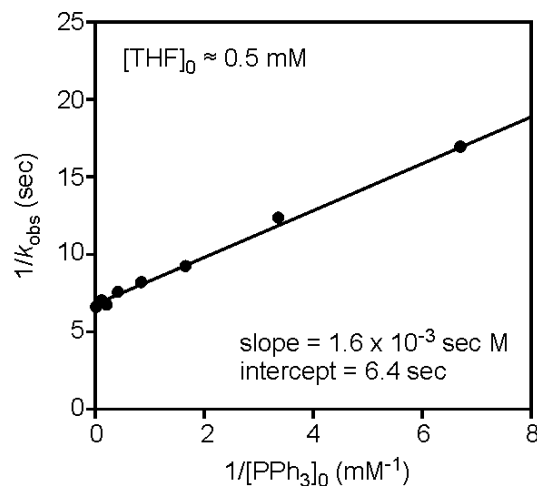
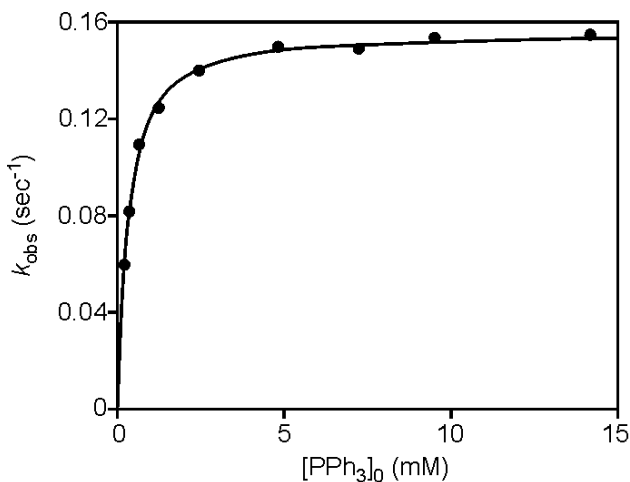


My abbreviations include chemistry,
but are a bit long; feel free to use your
own abbreviations for these species!

Mechanism 1:

Mechanism 2:

- b. The observed rates, and the measured pseudo-first order rate constants k_{obs} , increased with increasing PR_3 up to a saturation point, and decreased with added THF. Data for these experiments (using PPh_3 as the substrate) are shown below.



Which of your two mechanistic schemes is this data consistent with? In particular, look at the linear plots on the right; which of the rate laws you derived should exhibit these linear relationships? (Keep in mind that the data could be consistent with neither, one, or both mechanisms.)

- c. In each of the two mechanisms, which rate constants k would you expect to be influenced by the chemical character of PR_3 ? (In other words, if PR_3 was a better/worse ligand for Fe, was more/less nucleophilic, or was easier/more difficult to oxidize to OPR_3 , which rate constants would be affected?)
- d. At the saturation point in PPh_3 , the observed k_{obs} reached a maximum of 0.16 sec^{-1} (as shown in the upper left graph). The investigators found that this maximum did not vary with different substrates PR_3 (with $\text{R} = p\text{-C}_6\text{H}_4\text{Cl}$, $p\text{-C}_6\text{H}_4\text{F}$, $p\text{-C}_6\text{H}_4\text{CH}_3$, or $p\text{-C}_6\text{H}_4\text{OCH}_3$). Based on your answer to (c), which of the two mechanisms is more consistent with this data?

- e. From the data, estimate k_1 and k_2/k_1 . From a physical standpoint, what does k_2/k_1 represent?