

Cobalt-catalyzed Water Oxidation

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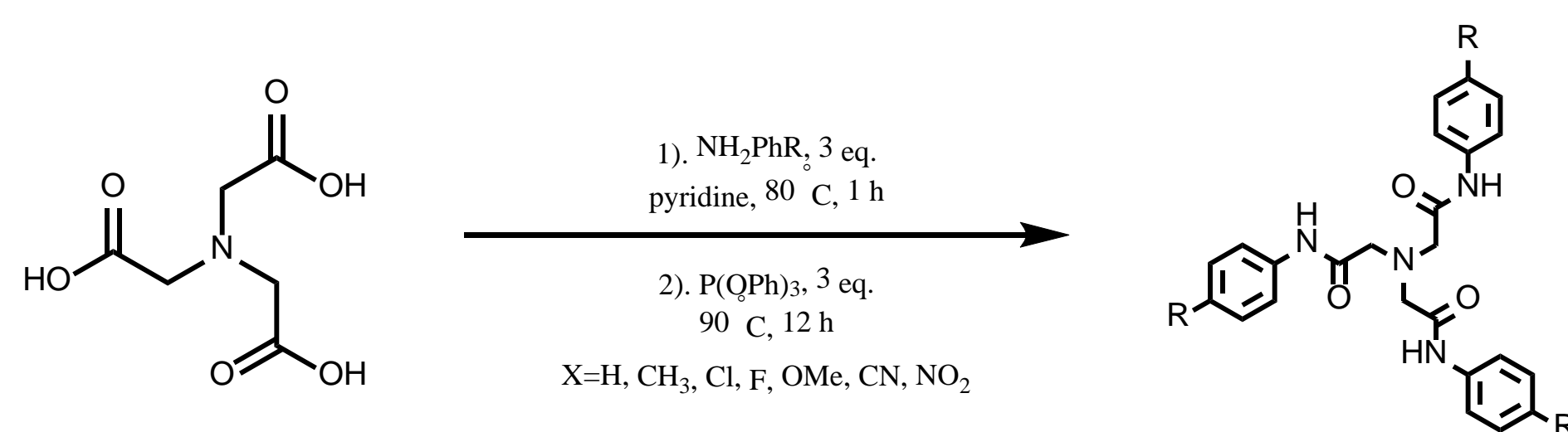
Introduction

Water oxidation is a naturally occurring process in nature, during photosynthesis. It also displays great potential for providing renewable energy via hydrogen. In the reaction, H₂O is oxidized to release oxygen gas, protons (H⁺), and electrons. However, the reaction is thermodynamically and kinetically slow.¹ Investigations are being conducted to develop an effective catalyst for this reaction using cobalt-based metal complexes, which have been met with some moderate success, albeit in a relatively inefficient manner. Many effective agents involve some type of cobalt and phosphate species, such as the one investigated by Nocera.² The catalyst was made from earth-abundant materials and operated in water in ambient conditions. The allure of developing an effective water splitting catalyst lies in the potential to provide clean energy. The evolved hydrogen and oxygen could be stored and combined again in fuel cells, etc.

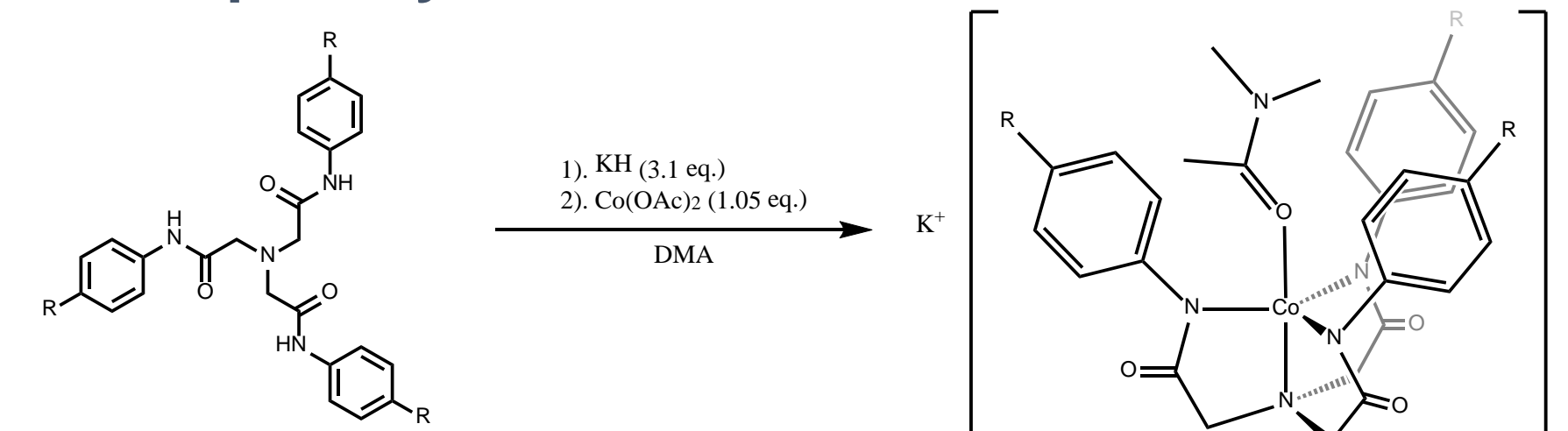
Methods

Ligand Synthesis*

Procedure taken from Borovik et. al.³



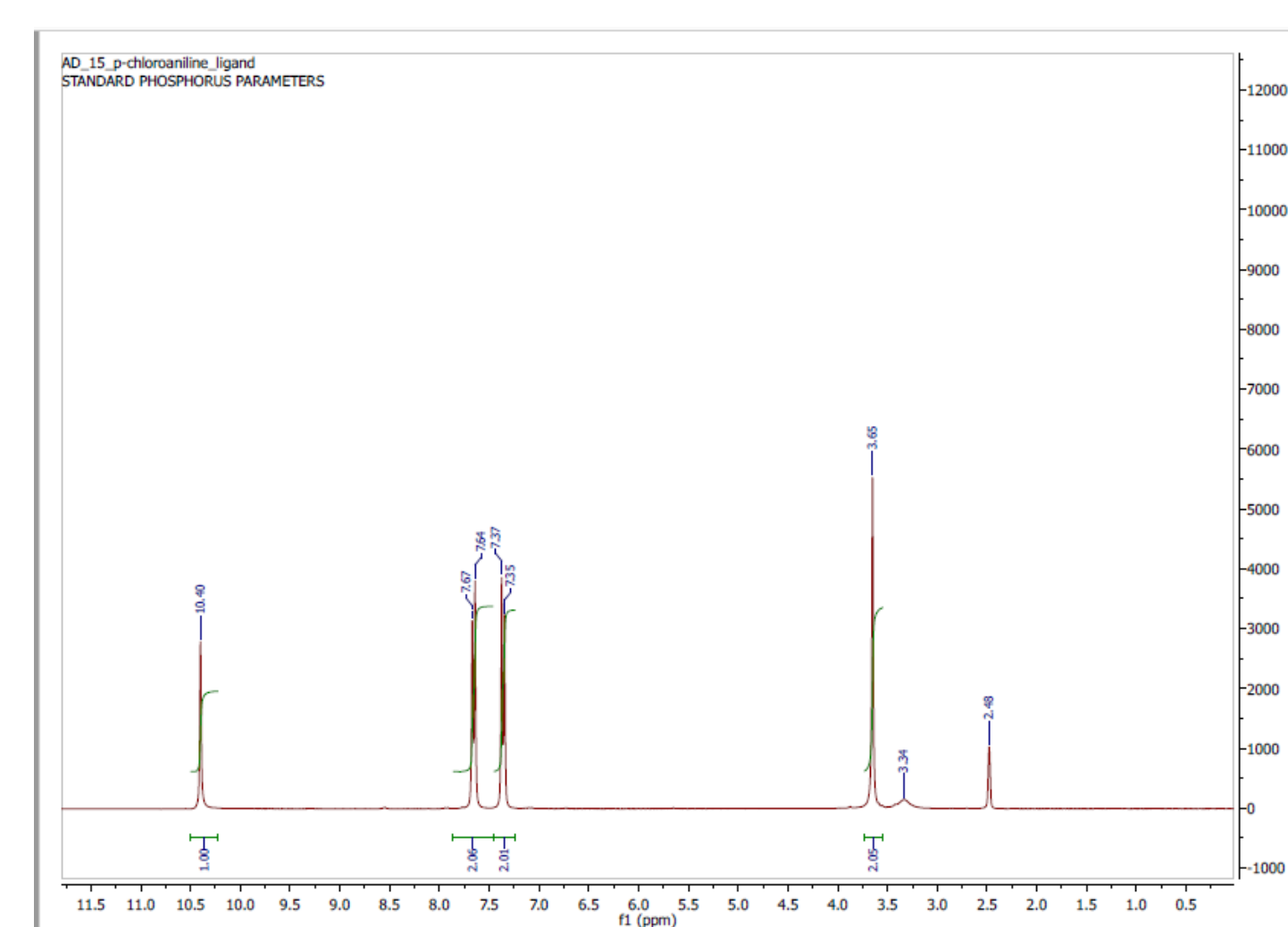
Complex Synthesis*



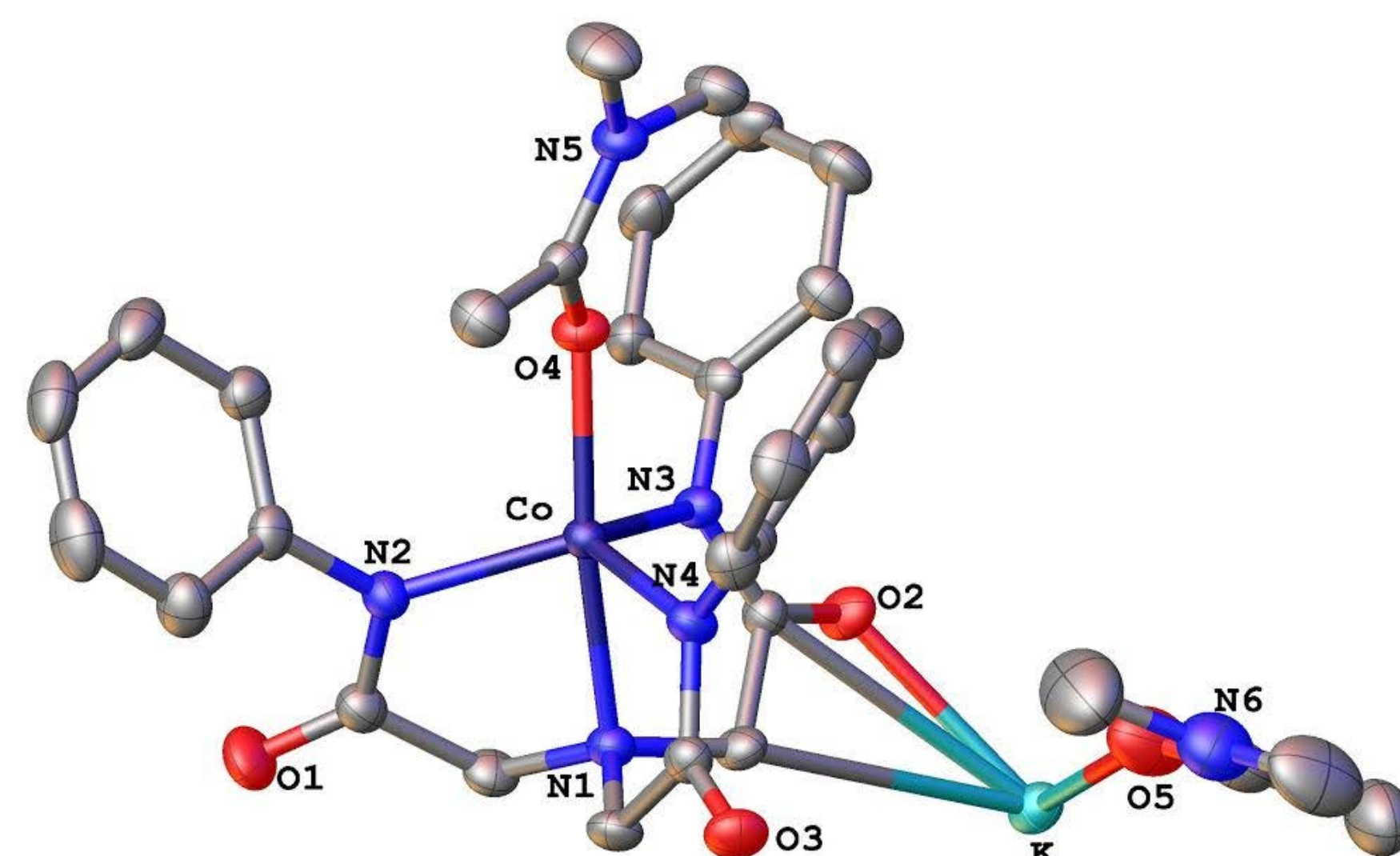
Note: All syntheses done in inert conditions (Schlenk line/glovebox)

Methods (cont.)

The ligand synthesis was confirmed using ¹H and ¹³C NMR as well as IR spectroscopy. An example proton NMR spectrum for tris(N-(p-chlorophenyl)carbamoylmethyl)amine is shown below.

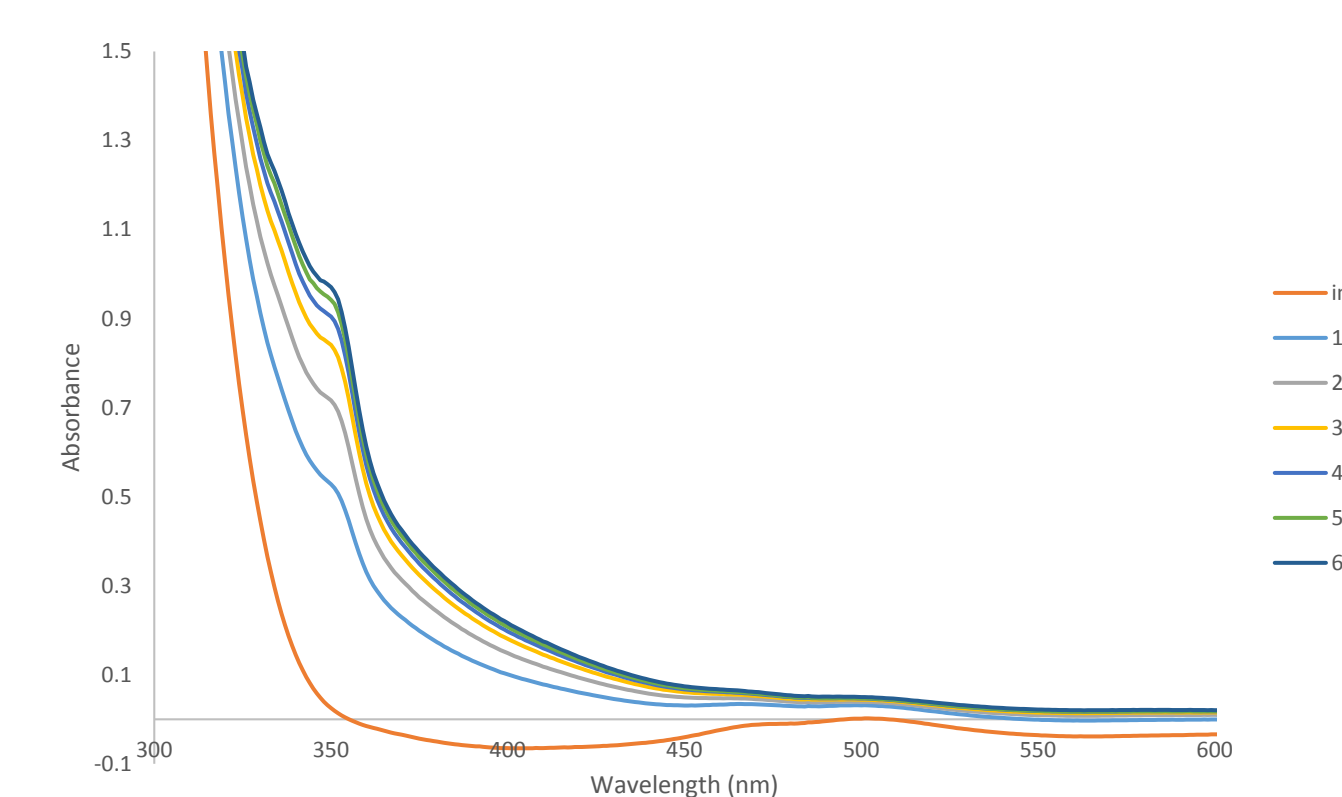


The cobalt complexes were characterized using XRD to determine crystal structure. A crystal structure for the cobalt molecule made from the tris(N-(phenyl)carbamoylmethyl)amine ligand is shown below. As seen in the reaction scheme in the Methods section, the complex itself is anionic and forms as a potassium salt. Recrystallation was performed both by layering and by vapor diffusion. Diethyl ether was used in both instances.

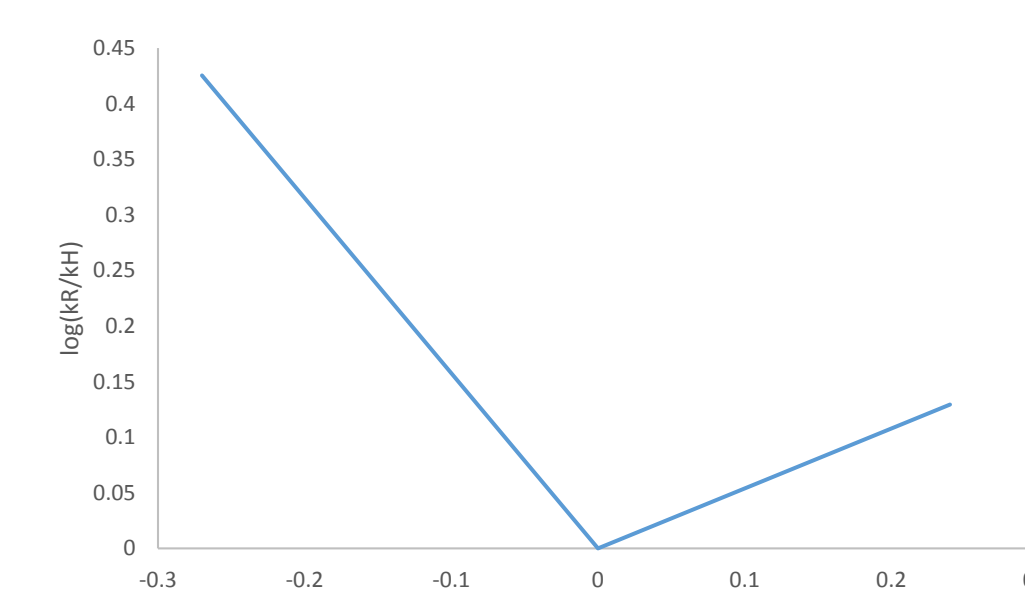


Results

The study conducted involved monitoring the effects of reacting cobalt complexes made from various ligands with hydrogen peroxide (via H₂O₂•2PPh₃ adduct). Solutions of complex with R = H, OMe, and Cl were prepared at .5 mM concentrations using serial dilutions. A stock H₂O₂•2PPh₃ solution was made at 75 mM in order to make additions of 1, 2, and 10 equivalents of the adduct. The reaction was tracked using UV-Vis spectroscopy with a scan taken every minute. The proposed reaction involves the cleavage of the O-O peroxide bond and the addition of a hydroxyl group to the cobalt complex. This process will cause either the oxidation of cobalt from II to III or simply increase the anionic character of the complex.



The spectra above are selected from the collected kinetics study. From the initial spectrum, each one is ten minutes apart. A new band clearly grows in around 350 nm, indicating the formation of a new substance. Using the kinetics data, the first order rate constants for the three reactions were calculated at 340 nm. This was used to generate a linear free energy relationship for the reaction.



P-substituent	k (s ⁻¹)	log(k ₀ /k _i)	σ
OMe	7.88E-03	0.425398	-0.27
H	2.96E-03	0	0
Cl	3.99E-03	0.129466	0.24

Clearly, the LFER generated from the experimental data is not completely linear. This relationship does indicate that there may be two separate steps of the overall reaction.

Conclusion

From the results of the kinetics studies on the three complexes, it is apparent that some product is being formed as a result of the reaction. To summarize:

- There was a color change from the initial pink solutions to a light yellow after the H₂O₂•2PPh₃ addition and elapsed time.
- While the LFER did not indicate a truly linear relation, it did show that there may be additional components to the reaction.
- If the catalyst was to be further examined, cobalt complexes with stronger electron withdrawing groups (EWGs) would be used to provide more points within the LFER..

Acknowledgements

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- All crystal structures were solved by Samantha MacMillan at Cornell University.
- Additional thanks to Anthony Cannella and Dr. Suman Dey for help with synthesis and characterization as well as solving crystal structures.

References

1. Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W., Molecular Catalysts for Water Oxidation. *Chemical Reviews* **2015**, *115* (23), 12974-13005.
2. Kanan, M. W.; Nocera, D. G., In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co²⁺. *Science* **2008**, *321* (5892), 1072-1075.
3. Ray, M.; Golombek, A. P.; Hendrich, M. P.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L.; Borovik, A. S., Structure and Magnetic Properties of Trigonal Bipyramidal Iron Nitrosyl Complexes. *Inorganic Chemistry* **1999**, *38* (13), 3110-3115.