Continuous Addition Kinetic Elucidation

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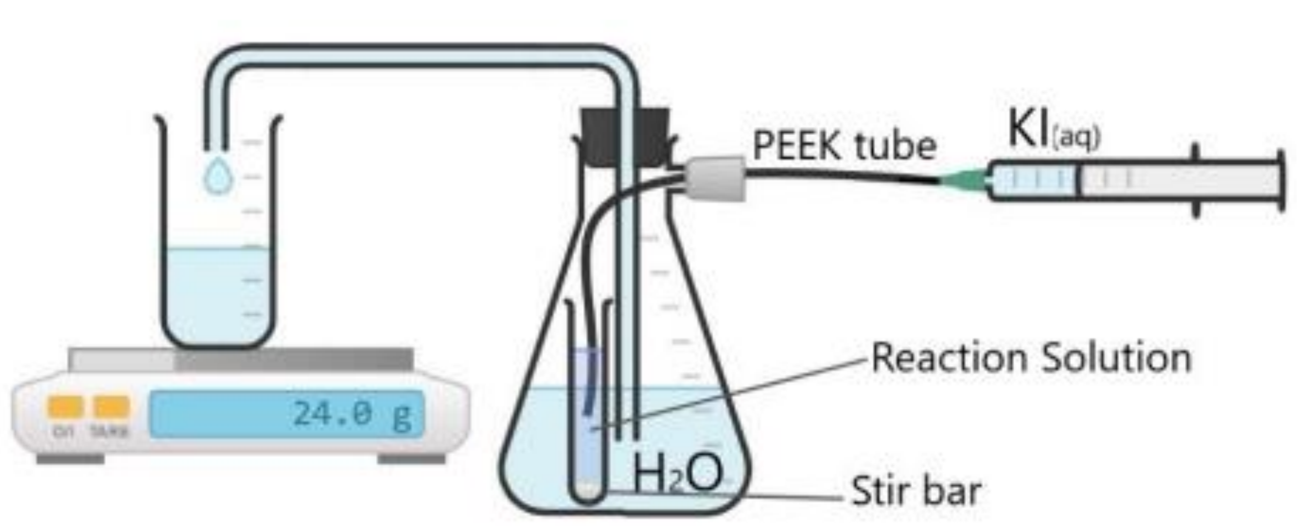
Introduction

- Kinetic analysis of catalytic reactions is time-consuming, as multiple reactions are required using various loadings and reactant concentrations. These are difficult to perform under identical conditions, and particularly challenging in the cases of catalysts that are air-sensitive and prone to degradation or poisoning. Continuous Addition Kinetic Elucidation (CAKE) involves the continuous injection of a catalyst while reaction progress is monitored.
- With CAKE, the plot of a reaction is only dependent on the order in reactant(s) and catalyst(s). This plot can be used to determine reactant and catalyst orders, the rate constant, and the amount of catalyst that has been poisoned.
- To test CAKE, the evolution of O_2 from KI-catalyzed H_2O_2 decomposition was studied.

Methods

- The set-up was assembled as shown below. H_2O_2 solution was placed in a test tube, which itself was placed within a Buchner flask. This flask was sealed, and catalyst solution tubes were inserted. The formation of O_2 inside the reaction vessel causes water to be ejected from the flask. The mass of ejected water is then used to calculate the amount of O_2 produced, allowing the reaction to be monitored with a photographic timelapse.

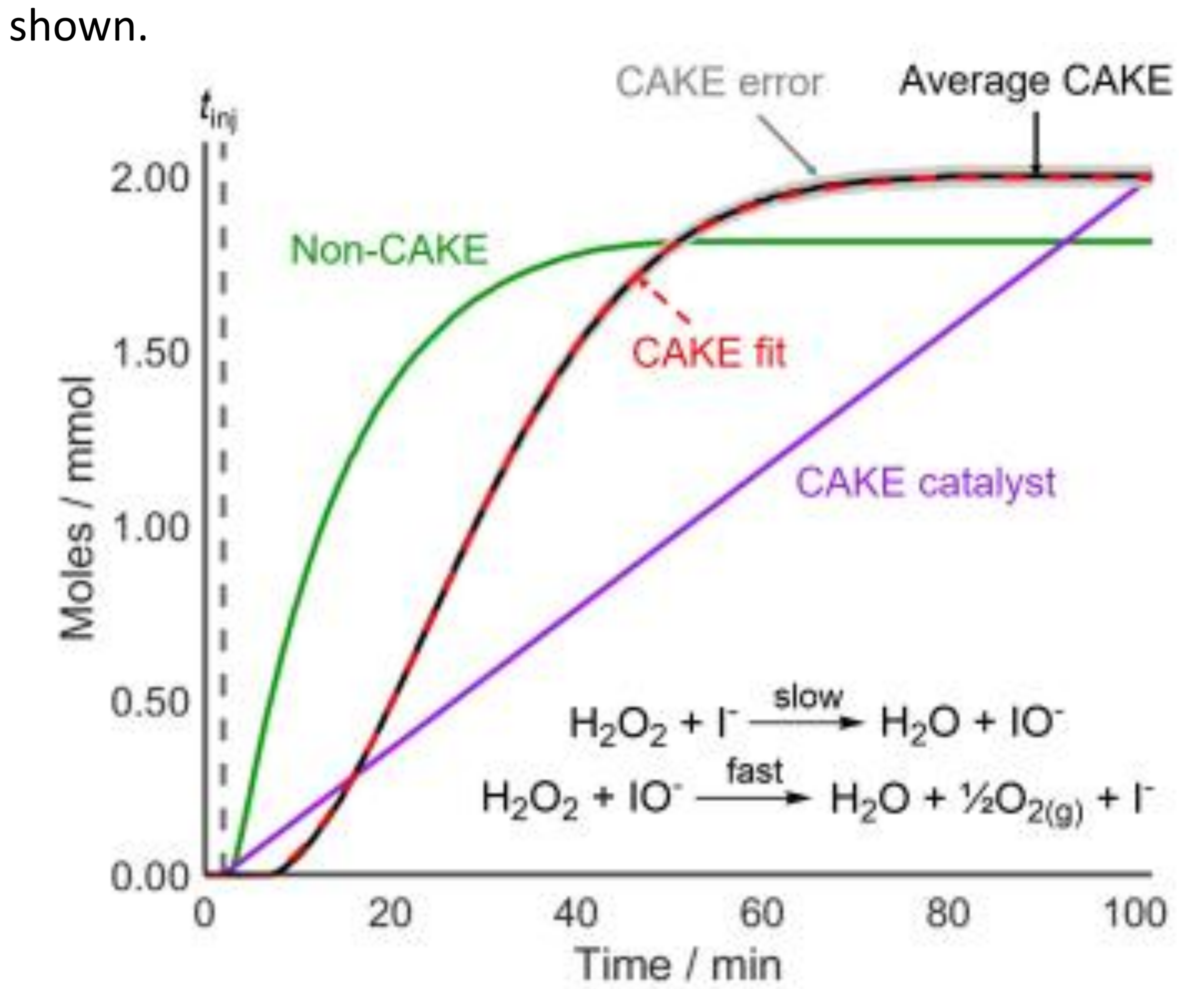


- CAKE reactions involving continuous addition of KI were performed, as well as non-CAKE reactions with a single addition of KI solution. Further experiments were performed with catalytically inactive KBr, and poisoning with $AgNO_3$.

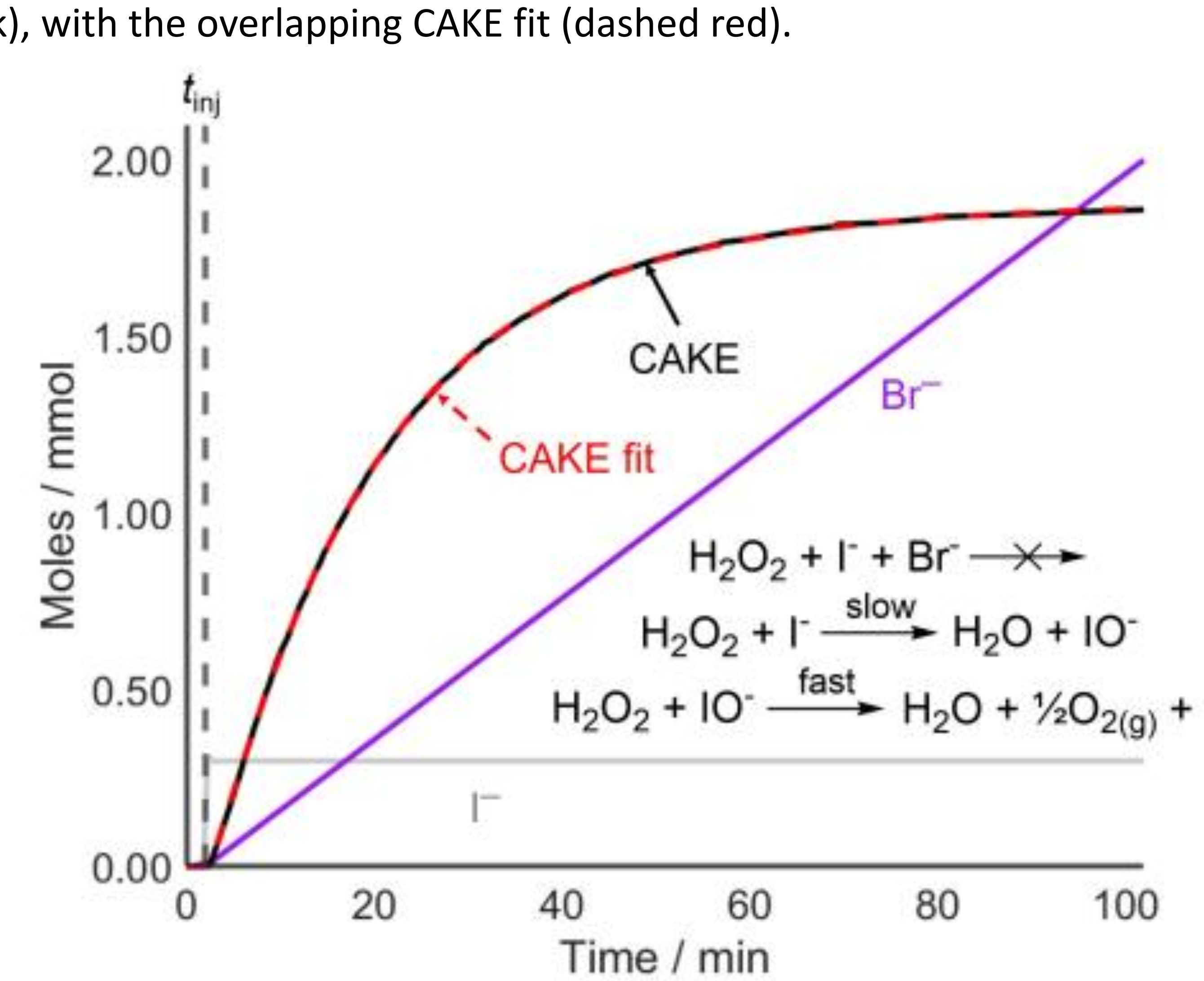
$$H_2O_2 \xrightarrow[H_2O]{\text{Catalyst(s)}\ \text{Additive(s)}} H_2O + \tfrac{1}{2}\, O_2$$

Reaction Orders

- Non-CAKE and CAKE reactions show distinct plot shapes, which are only dependent on the order of the reactant and catalyst.
- Catalyst is consumed quickly in the non-CAKE reaction, due to the single addition of KI at 2 minutes. The CAKE reaction initially was slow, but increased as KI was continually injected.
- The reaction was shown to be first order in reactant and catalyst (1.11±0.01 and 1.18±0.03), which is the most common case for catalytic reactions. A rate constant of 0.008±0.001 $M^{-1}\,s^{-1}$ was obtained, which is comparable to the literature value of 0.0176±0.0017 $M^{-1}\,s^{-1}$. The graph below shows experimental data (black), the error region (grey), and the CAKE fit (dashed red). CAKE catalyst and a non-CAKE experiment are also shown.

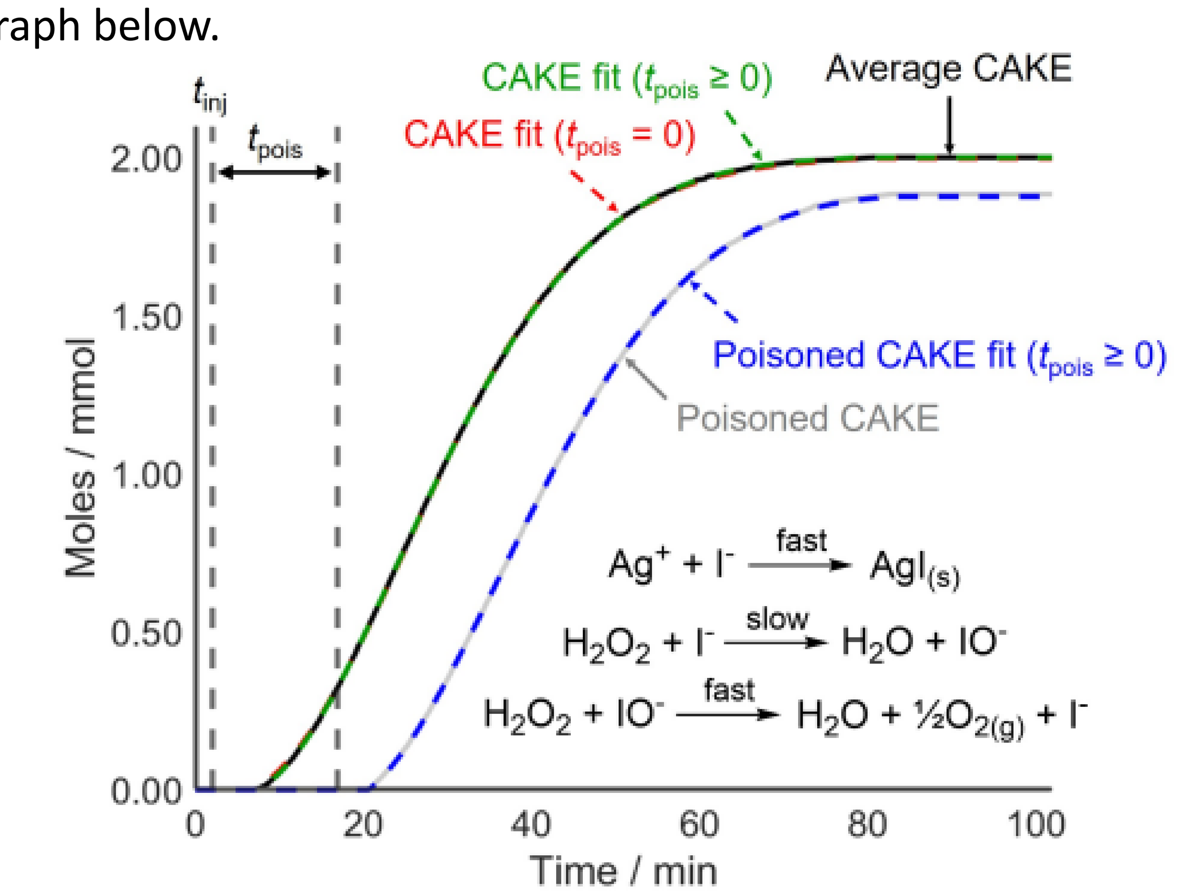


- A non-CAKE KI reaction was performed with the continuous injection of KBr to examine different orders.
- It was shown that Br^- exhibited zero order behaviour (0.13±0.01), while the H_2O_2 reactant was first order (1.20±0.01). The graph below shows the experimental data (black), with the overlapping CAKE fit (dashed red).



Poisoning

- Organometallic catalysts and enzymes are particularly prone to poisoning, and uncertainty arises during very low catalyst loadings.
- With CAKE, limited amounts of catalyst are initially present, which delays the start point of the reaction until the poison has been consumed. This is shown in the graph below.



- Upon continuous I^- addition, AgI precipitates and effectively inactivates I^- as a catalyst. The orders in reactant and catalyst (0.985±0.004 and 0.835±0.008) are similar to reactions that were not purposely poisoned.
- The poisoned experiment has a delayed start due to the presence of Ag^+ poison, although the start time of ~14.9 minute was larger than the anticipated 10 minute delay. When non-poisoned reactions were examined, a ~3.5 minute delay was obtained. This suggests that poison was present in both reactions, and this gives a more accurate ~11.4 minute delay.

Conclusion

- CAKE efficiently determines the order in reactant and catalyst in a single reaction. It improves reproducibility concerns, and accounts for reactions that are prone to poisoning. It is a simple, powerful approach to kinetic elucidation with advantages over traditional approaches to similar kinetic reactions.
- Future work will investigate multiple reactant systems and excess catalyst systems.

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Citations

P. Williams, C. Killeen, I. Chagunda, B. Henderson, S. Donnecke, W. Munro, J. Sidhu, D. Kraft, D. Harrington, S. McIndoe, *Continuous Addition Kinetic Elucidation: Catalyst and Reactant Order, Rate Constant, and Poisoning from a Single Experiment*, Chemistry, **2022**.

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