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Laboratory Experiment

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Kinetics, Reaction Orders, Rate Laws, and Their Relation to Mechanisms: A Hands-On Introduction for High School Students Using Portable Spectrophotometry

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S Supporting Information

ABSTRACT: Teaching complex chemistry concepts such as kinetics using inquiry−based learning techniques can be challenging in a high school classroom setting. Access to expensive laboratory equipment such as spectrometers is typically limited and most reaction kinetics experiments have been designed for advanced placement (AP) or first-year undergraduate courses. Therefore, we developed a new and inexpensive laboratory experiment specially tailored for high school students. The activities include in situ monitoring of iodide oxidation using individual UV−visible spectrophotometers, data analysis with a spreadsheet, and interpretation. The experiment introduces chemical kinetics, offers practice problems, and teaches students the technique of flooding to acquire data and make connections with reaction mechanisms based on trends observed in the rate constants. The exercise was successful in solidifying the concepts of rates, rate laws, reaction order, and their relation to mechanistic studies. The provided handout and notes are tailored to help high school science teachers implement the Next Generation Science Standards in their classrooms.

KEYWORDS: *High School/Introductory Chemistry, Analytical Chemistry, Laboratory Instruction, Physical Chemistry, Hands-On Learning, Inquiry-Based/Discovery Learning, Kinetics, Mechanisms of Reactions, Rate Law, UV−Vis Spectroscopy*

■ INTRODUCTION

Teaching chemical kinetics at the high school level offers an excellent opportunity for students to combine hands-on experiments with mathematical and computational thinking.[1] The student's experimental skills are improved as they need to carefully measure volumes of reactants and reaction times. In addition, they understand the effects of concentration and temperature on reaction rates, propose and test predictions, acquire and model data, revise their hypotheses based on experimental evidence, and eventually identify the laws that govern the studied reaction.[1] Studying chemical kinetics also provides high school teachers with a unique opportunity to cover a broad range of scientific and engineering concepts essential to the Next Generation Science Standards.[2,3] However, teaching chemical kinetics at the high school level is particularly challenging. Experiments already available in the literature were primarily designed for undergraduate courses.[4−7] They often require expensive equipment, complex software,[5] advanced experimental and mathematical skills,[6] and require multiple class periods. Several chemical kinetics laboratories were tailored for high school students but they either consist in overhead projector demonstrations[4] or in relatively basic experiments,[8] which do not allow students to go through all the steps involved in scientific reasoning. A recent investigation also determined that science teachers present significant misconceptions due to insufficient training on this topic.[9,10] Among these misconceptions were how reaction rates change as a function of time, the concept and number of rate limiting steps, and the relationship between enthalpy and reaction rates. To address these challenges, we designed a kinetics laboratory together with a high school chemistry teacher from the ground up. Our goal for this lab was to engage students through hands-on experimentation, expose them to in situ characterization techniques, develop their scientific reasoning skills using inquiry-based learning techniques, and provide them with strong foundations on chemical kinetics. At the same time, this lab takes into account the time and cost constraints inherent to high school teaching.

■ EXPERIMENTAL OVERVIEW

Laboratory experiments developed for high schools typically target real-world issues and expose students to cutting edge research as part of an outreach effort. The motivation for these laboratories is to generate enthusiasm among students and encourage them to consider a career in STEM fields. Although tremendously important, these experiments typically require

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multiple (often 3−5) class periods and, in practice, teachers can only accommodate one of these laboratories per semester due to time constraints and difficulty to insert them in the curriculum. Our interactions with high school science teachers revealed a need for shorter laboratories, of 50 to 100 min, which would address several Next Generation Science Standards (NGSS) and expose students to scientific reasoning though inquiry-based learning.

The described laboratory offers an introductory explanation of kinetics and a guided question sets to help students make the connections between kinetic studies and reaction mechanisms. It starts out with a typical explanation of reaction rates, order of reaction, and rate laws and then introduces the concept of flooding so that mechanistic information can be gathered from the observed rate constants. In the following experimental part, students reinvestigate the work of Liebhafsky and Mohammad on the kinetics of iodide (I^-) oxidation by hydrogen peroxide (H_2O_2).[11] The authors studied the previously reported accelerating effect of acid on this reaction (eq 1) and proposed parallel pathways by which this reaction occurs

$$H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O \quad k_{obs} \tag{1}$$

Here, the students' experiment has been modernized through in situ monitoring of colorimetric changes due to the formation of yellow triiodide (I_3^-) product. The exercise is designed around the portable Vernier SpectroVis Plus spectrophotometer, which is available for purchase at a reasonable cost for most high schools. Data is then tabulated and plotted in Excel, and a rate law consistent with the proposed mechanism is obtained. This experiment has been tailored to address several NGS standards in a single experiment: students study the effects that changing concentration has on reaction rates (HS-PS1-5), they understand that a "dynamic and condition-dependent balance between a reaction and the reverse reaction determines the number of all molecules present" (HS-PS1-6), they analyze data from in situ reaction monitoring and develop simple mathematical models to identify and support claims on reaction orders (HS-PS1-4 and HS-PS1-7).

■ EXPERIMENT

This laboratory exercise requires teachers to prepare stock solutions of 0.75 M KI (CAS # 7681-11-0), 1.2 mM H_2O_2 (CAS # 7722-84-1), and 0.6 M HNO_3 (CAS # 7697-37-2) in advance. Detailed instructions to prepare these solutions are provided in the Supporting Information. The kinetics for the reaction between I^- and H_2O_2 are monitored in situ using Vernier Software & Technologies LabQuest units equipped with the SpectroVis Plus spectrophotometer accessory. These portable spectrophotometers were specially developed for educational and outreach activities. They are simple to use and their cost is similar to a tablet, which makes them affordable for most schools. Ideally, one spectrophotometer should be provided to each group of students. However, data collection is fast, and we noticed that one or two SpectroVis Plus units are sufficient for a class. Students will also need standard disposable or quartz cuvettes, liquid measuring apparatuses (preferably plastic syringes, but eye droppers will work), and access to a computer equipped with Microscoft Excel.

There are seven sets of experimental conditions. It is recommended that one set of conditions be assigned per student or group, so that data collection is limited to 30 min. Students first set their Vernier LabQuest following the instructions in the provided handout (Supporting Information). They then retrieve aliquots of the stock solutions and mix them in a cuvette according to the assigned experiment. The last reagent to be added is H_2O_2, followed by capping and inverting the cuvette to mix the reagents. The cuvette is then placed in the SpectroVis Plus accessory for collection of the kinetic trace. Upon completion of data collection, the students use the preprogrammed fitting software to determine the observed rate constant (k_{obs}) for their set of conditions. All students or groups then add their k_{obs} in a class Excel spreadsheet and complete the guided analysis questions. These questions require students to draw conclusions about the order of the reactions with respect to each species, identify a rate law that is consistent with their observations, and do algebraic manipulations to calculate elementary rate constants for the given kinetically observed elementary reactions. If so desired, students can be asked to find the original article and compare their rate constants. *Note: Students will calculate their rate constants in units of* M^{-1} *sec*$^{-1}$ *and* M^{-2} *sec*$^{-1}$*, but the original manuscript provides values of* M^{-1} *min*$^{-1}$ *and* M^{-2} *min*$^{-1}$*.*

■ HAZARDS

Solutions of HNO_3 are corrosive. H_2O_2 is an oxidant and is corrosive. Iodide salts have been reported to cause harm to unborn children. Appropriate personal protective equipment (gloves, lab coats, and eye protection) should be worn at all times. High concentration solutions should be disposed of following specific site, district, and state protocols. However, the small volumes of low concentration solutions used for the lab do not need any special attention as 3% H_2O_2 is a common disinfectant and KI is a food additive. Plastic syringes (without needles) offer a safe and accurate way to dispense small amounts of stock solutions in the cuvettes.[12] They are economical, unbreakable, reusable, and reduce the risk of spill compared to burets and graduated cylinders.

■ RESULTS AND DISCUSSION

This laboratory exercise was carried out in a high school chemistry classroom with approximately 20 students in groups of 3 and required between 50 and 100 min for completion. Students were given the handout (Supporting Information) ahead of time and were asked to read the prelab section and answer the questions 1−3 to test their understanding. The lab period started with a short overview and discussion on these concepts. In general, students found the theoretical prelab section adequate in length and difficulty. The linear increase of the observed rate constant with increasing reactant concentration was trivial. However, zero and second order reactions were new and students found the provided graphs to be very helpful to understand the impact the reaction order has on the observed rate constant.

For the experimental part of the lab, students followed the detailed procedure provided in the handout. Although the level of details seems to give little freedom for students to experiment, it allowed to dedicate more time to data analysis, interpretation, and discussion of the reaction mechanisms as a group. Overall, students liked to have detailed instructions as it was the first time they used the LabQuest and SprectoVis Plus instruments. The analogy between the SpectroVis Plus unit and their own eyes generated a lot of excitement and discussions as students were able to put scientific data (values!)

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on a color change they witnessed. From their observations, the class was able to make connections about the relationship between the reaction rate and the color of the solutions in the vials. Students also liked to go through all the steps of scientific inquiry, including modeling the data and proposing a reaction mechanism based on the observed trends.

Students expressed interest in the laboratory and left with a better understanding of kinetics, reaction orders, rate laws, and their relation to mechanisms. The knowledge and skills gained during this exercise facilitated an open classroom discussion on the effects of addition of catalysts, surface area, temperature, and pressure on rates of reactions. Additionally, the elementary rate constants calculated by following the outlined procedure (k_2 = 0.0107 M^{-1} s^{-1} and k_3 = 0.170 M^{-2} s^{-1}) were quantitatively similar to the published values (k_2 = 0.0115 M^{-1} s^{-1} and k_3 = 0.173 M^{-2} s^{-1}); see eq 2–3.[11]

$$H_2O_2 + I^- \rightarrow H_2O + IO^- \quad k_2 \tag{2}$$

$$H_2O_2 + H^+ + I^- \rightarrow H_2O + HIO \quad k_3 \tag{3}$$

More importantly, this laboratory provides students with hands-on in-depth learning of chemical kinetics and their relation to reaction mechanisms; the learned concepts are critically important for the optimization of industrial processes, catalyst development, understanding of biological processes, medicine, environmental science, and other areas.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00640.

Instructor's notes to prepare the stock solutions, general teacher notes, additional resources, and handout with answer key. (PDF)

Instructor's notes to prepare the stock solutions, general teacher notes, additional resources, and handout with answer key. (DOCX)

Student handout with detailed experimental procedures for data acquisition and guided analysis questions. (PDF)

Student handout with detailed experimental procedures for data acquisition and guided analysis questions. (DOCX)

Excel spreadsheet for data analysis. (XLSX)

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Notes

The authors declare no competing financial interest.

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