The Blue Bottle Reaction as a General Chemistry Experiment on Reaction Mechanisms

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Background

The blue bottle reaction is a widely known and popular demonstration in chemistry classes and chemistry magic shows (1). At Valparaiso University it has been used for many years in our general chemistry laboratory as an experiment in chemical kinetics illustrating the determination of a reaction mechanism. Most general chemistry laboratory manuals include a few experiments on kinetics, but none involving reaction mechanisms. Our version of this experiment was inspired by an article by J. A. Campbell in this *Journal* in 1963 (2) and by his discussion of the reaction in a later book, "Why Do Chemical Reactions Occur?", published in 1965 (3). In the article, and in Chapter 2 of the book, Campbell analyzes the blue bottle reaction, and through a series of experimental observations obtains the mechanism for the reaction. Our experiment consists of a series of procedures and questions where each observation prompts a new question, each question leads to a hypothesis, and each hypothesis leads to more questions and experiments. Eventually, a preliminary mechanism is proposed, then tested with additional experiments and questions. As a result, the preliminary mechanism is modified to give the final mechanism.

Thus, this experiment not only illustrates a reaction mechanism but also is an excellent example of the scientific method. It is especially valuable in this regard because the students discover that their initial hypotheses are not always supported by experiment and must be changed or discarded. Sometimes students are reluctant to change their ideas of what must be occurring in the reaction, even in the face of evidence to the contrary.

With this format, this experiment is quite different from most experiments in the general chemistry laboratory. It forces the students to think about each step before going on to the next one. It is not an experiment where they can just collect the data and go home. While some students are initially irritated by this approach, and some are frustrated that they don't understand the reaction immediately, by the end of the class period they feel that they have really accomplished something. In course evaluations this experiment is often cited as the favorite experiment of the year, and many students remember and comment on it years later.

This experiment is also more demanding on the laboratory instructor. Over the years we have found that the instructor must be actively involved in the discussions of the students, to help them out when they get stuck and to keep them on the right track. Most students are not able to make the final interpretation of the results without assistance. For these reasons we have designated a few stopping points in the procedure, where the instructor checks that the students are on the right track. These stopping points can be a time for the class as a whole to discuss the results and compare hypotheses, or if the class is small enough the instructor can work with each group individually.

The Experiment

In the blue bottle reaction, dextrose ($\alpha\text{-D-glucose}$) is added to an aqueous solution of NaOH, along with a small amount of methylene blue. When the solution is shaken, it turns blue. After standing a short time, the solution fades to colorless. The process can be repeated many times. The experiment has a series of questions that lead the students to discover that:

- 1. The shaking introduces oxygen into the solution.
- The oxygen reacts with something in the solution (later found to be a catalyst) to form a blue intermediate.
- The blue intermediate reacts with something else in the solution to form a colorless product.
- 4. The change from blue to colorless is *not* the reverse of the change from colorless to blue.
- Shaking the solution for a longer time causes the reaction to take longer, but doesn't make it any bluer.
- 6. Because the solution reaches a certain level of blue and doesn't get any bluer regardless of how much it is shaken, one of the reactants is being used up, and therefore must be a catalyst (because the process can be repeated).
- The constant intensity of the blue color means that for most of the time during the reaction, the colorless-toblue step is occurring simultaneously with the blueto-colorless step.
- The shaking step is not the same as the colorless-toblue step, but serves to produce aqueous oxygen from gaseous oxygen.
- The variable length of the reaction is due to the variable amount of oxygen dissolved in the solution by changing the number of shakes.
- 10. There are actually 3 steps to the reaction, not 2.

Common erroneous hypotheses that must be discarded are:

- The shaking is adding energy to the solution, which initiates the reaction.
- 2. The purpose of the shaking is to mix the reactants.
- 3. The blue-to-colorless step is simply the reverse of the colorless-to-blue step.
- More shaking produces more blue intermediate, and that's why the reaction lasts longer.
- 5. There are 2 steps in the mechanism, and they are sequential.

Discussion

The goal of the experiment is to deduce the mechanism of the reaction, using letters instead of chemical formulas. The actual mechanism for the reaction is given by Campbell (2, 3) and by Summerlin and Ealy (1). In the reaction, the glucose reacts with the NaOH to form the glucoside. The methylene blue is oxidized to its blue form by O_2 . The glu-

coside is then oxidized by the blue form of the methylene blue. The mechanism that the students discover is:

$$A(g) \rightarrow A(aq)$$

 $A(aq) + B \rightarrow C$
 $C + D \rightarrow E + B$

Where $A = O_2$, B = methylene blue (colorless), C = oxidized methylene blue (blue), D = glucoside, and E = oxidized glucose.

Although the presence of the NaOH cannot be observed in the experiment, it can also be shown to affect the rate if more experiments are done with different NaOH concentrations. If desired, it is also possible to do the reaction at different temperatures to show that temperature affects the rate of a reaction, or to determine activation energy. Heating the reaction accelerates the decomposition process, though, so care should be taken when increasing the temperature. Also, research here at Valparaiso University, reported in a previous article in this Journal (4), has shown that other sugars and other dyes can be used, giving different rates and different colors for the reaction.

Most of our experience with this experiment has been with first-year general chemistry students, and it is written for that level. It has also been done at a workshop relating to critical thinking for college faculty, and with high school students at an academic summer camp at Valparaiso University. Recently, an abbreviated oral version of this experiment was used with a middle school (junior high) science class. This class had some trouble with chemical reaction mechanisms and the idea of reactants, products, catalysts, and intermediates. However, they did understand the application of the scientific method used in the experiment.

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Note

WThe student version of this experiment and the instructor version with notes are available on JCE Online at http://jchemed.chem.wisc.edu/ Journal/issues/1999/Nov/abs1519.html.

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