A Student Laboratory Experiment Based on the Vitamin C Clock Reaction

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We have adapted the "Vitamin C Clock Reaction" tested demonstration *(1)* to serve as a student laboratory experiment in high school or college-level general chemistry. The rate of the reaction shown in eq 1 is measured at varying concentrations of hydrogen peroxide and iodide ion, so that the method of initial rates can be used to determine the rate law.

$$H_2O_{2(aq)} + 3I^-_{(aq)} + 2H^+_{(aq)} \rightarrow I_3^-{}_{(aq)} + 2H_2O \quad (1)$$

This is one of the earliest reactions to be subjected to a systematic kinetics investigation *(2)* and has been the subject of several demonstrations *(3)* and student experiments *(4–6)*.

The reaction occurs at low pH, with a mechanism that involves formation of OI^-:

$$H_2O_{2(aq)} + I^-_{(aq)} \rightarrow OI^-_{(aq)} + H_2O \quad (2)$$

We avoid higher pH values, where H_2O_2 can act as a reducing agent:

$$H_2O_{2(aq)} + OI^-_{(aq)} \rightarrow I^-_{(aq)} + H_2O + O_2 \quad (3)$$

The sum of eqs 2 and 3 amounts to the decomposition of H_2O_2 catalyzed by iodide, which competes with the oxidation of iodide at higher pH.

In the vitamin C clock variation, no iodine product of reaction (1) accumulates until a small quantity of added vitamin C is depleted. As iodine is produced (as the triiodide ion) in reaction (1), it is consumed by vitamin C (ascorbic acid) according to eq 4 to give 2,3-diketogulonic acid:

$$I_3^-{}_{(aq)} + C_6H_8O_{6(aq)} + H_2O \rightarrow 2H^+_{(aq)} + 3I^-_{(aq)} + C_6H_8O_{7(aq)} \quad (4)$$

When the vitamin C is finally depleted, the triiodide ion accumulates and it may be detected by use of starch indicator.

Reaction (1) has been demonstrated to follow the rate law

$$\frac{d[I_3^-]}{dt} = k_1^0[H_2O_2][I^-] + k_1[H_2O_2][I^-][H^+] \quad (5)$$

under conditions where $[H_2O_2] < [I^-]$ and $[H^+] \cong [I^-]$ *(2)*. Then $k_1^0 = 0.69\ M^{-1}\ min^{-1}$ ($0.012\ M^{-1}\ s^{-1}$), $k_1 \cong 10.5\ M^{-2}\ min^{-1}$ (both at 25 °C), and the activation energy for the bimolecular reaction is 56 kJ/mol. We used slightly different experimental conditions, and since this reaction system is exceedingly complex *(7)*, we were surprised to find reasonable agreement with the published values (although there was wide variation in student results). We used a moderate pH of ~2.3–2.4 where the second term in eq 5 should contribute minimally to the total rate *(2)*, but made no attempt to control or measure the pH during the reaction, other than adding acetic acid so that its concentration was substantially greater than that of the reactants. Neither $[I^-]$ nor $[H^+]$ changes significantly during the reaction because they are consumed and produced in equal quantities by eqs 1 and 4, and the vitamin C concentration is held low enough so that only 1–3% of the hydrogen peroxide is consumed during the stage of the reaction used to determine the rate.

Experimental Procedure

It is easy, and possibly desirable in a high school setting, to do this experiment with no equipment except a stopwatch with which to time the color change. However, all of our general chemistry laboratory experiments are run from Excel templates with a strategy we call LIMSport *(8)*. Templates include links to various data acquisition programs[1] so data are easily imported into the spreadsheet where they can be manipulated with standard techniques. In the present case, because the Vernier Lab Pro hardware[2] is probably the most convenient and popular option, we have linked a Logger Pro setup (.CMBL) file. Clicking on the link in Excel automatically opens LoggerPro with the recommended data acquisition settings as defaults. An interfaced colorimeter is used to acquire absorbance measurements about every 4 seconds, and these are plotted as a permanent record of the time at which the starch–iodine complex appears. Using the colorimeter ensures that the time of the indicator change will not be missed (it was very easy to detect the first increase above baseline) and documents the time of color change in printable data. The Excel template expedites tedious repetitive calculations.

We used consumer products exclusively because we thought that approach made the experiments more interesting and relevant to students' experience. The procedure involves crushing and dissolving a 500 mg vitamin C tablet, diluting the solution to the mark in a 50 mL volumetric flask, and adding 5.0 mL of the solution and 2.0 mL of tincture of iodine to a 25 mL volumetric flask, then diluting to make solution A. Solution B is made by diluting 17 mL of 3% hydrogen peroxide and a few milliliters of starch solution to 25 mL, and solution C is commercial white vinegar. These solutions are mixed in various proportions so that the rate law can be deduced from the data.

Because we do not want students to miss the forest of kinetics for the trees of experimental detail, we make several procedural concessions:

1. We prepare solutions directly in disposable spectrometer cuvettes by means of 3 mL syringes (without needles). This may lead to low precision, as well as the theoretically important (but insignificant in practice) error in concentrations resulting from nonadditivity of volumes. Training students to use syringes, including methods of eliminating bubbles, can improve results.

2. We suggest a determination of the apparent activation energy, E_a, by immersing a capped syringe with one ingredient, and capped cuvette with the rest, in a constant temperature bath that includes a temperature probe. They are removed, the syringe contents are injected into the cuvette, and after the absorbance is measured in the usual way, the temperature is measured again. The average of the two temperatures is used, along with data from a room temperature run, to estimate E_a. There is a temperature change of several degrees, leading to some error.
3. We time each run from the beginning of data acquisition, even though it may take students a few seconds to add the final reagent to the cuvette, insert it in the colorimeter, and start measurements. Since total times are around 100 s, this is a relatively small error, especially with students working in pairs so that they can cooperate in carrying out the operations.
4. We have kept to the philosophy of using consumer products only. The use of acetic acid minimizes the dependence of the rate on the hydrogen ion concentration *(2, 9)*. We felt that it is not desirable to complicate this basic experiment further, and since an increase in pH leads to a complex mechanism, it is more appropriately studied in advanced courses. We make our own tincture of iodine because the commercial material is expensive, but we leave a bottle of commercial product out.

Hazards

Tincture of iodine contains inflammable ethyl alcohol, toxic iodine, potassium iodide, and water. I_2 is a minor skin irritant, and prolonged exposure may cause staining burning. The tincture should not be vaporized by heating because iodine vapor is a respiratory irritant. Excess solution should be reduced with vitamin C before disposal.

Results

Average results of 25 student trials (50 students working in pairs), with standard deviations in parentheses, were as follows: order with respect to H_2O_2: 0.94 (±0.27); order with respect to I^-: 1.05 (±0.24); k: 0.017 $M^{-1}s^{-1}$ (±0.007) at 22.3 °C (±0.63 °C); E_a = 51.3 kJ/mol (±20.1 kJ/mol). We take the agreement of averages with known values as validation of our procedure, and large variances as evidence that students ran the reaction at slightly different temperatures, that they may not have completely dissolved the vitamin C, and may have benefited from more instruction on volume measurements with syringes.

Supplemental Materials

Student instructions with details of solution preparation, Excel template, and WebCT prelaboratory questions (both as a native WebCT file and MS Word document) are available in this issue of *JCE Online*.

Notes

1. Various assembly language or compiled routines have been used, and Visual Basic macros have been used to link LabView routines to import data from National Instruments data acquisition devices. See citations in ref *7*.

2. Vernier Software and Technology, 13979 SW Millikan Way, Beaverton, OR 97005-2886, 888/837-6437; *http://www.vernier.com* (accessed Mar 2007).

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