

Tested Demonstrations

edited by

Ed Vitz

Kutztown University
Kutztown, PA 19530

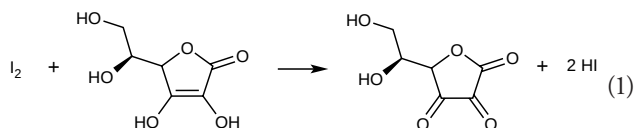
The Vitamin C Clock Reaction

submitted by: **Stephen W. Wright**Pfizer Global Research and Development, Groton, CT 06340; stephen_w_wright@groton.pfizer.comchecked by: **Phil Reedy**

Department of Chemistry, San Joaquin Delta College, Stockton, CA 95201

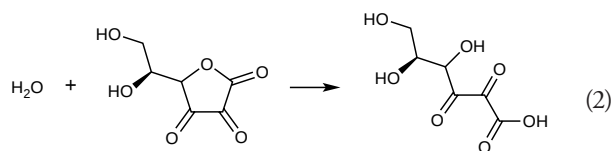
Clock reactions are a perennial favorite among chemical demonstrations, with their bright colors and abrupt changes. Unfortunately the number of chemical systems that successfully produce a clock reaction effect is relatively small. The Landolt iodine clock reaction (1), which uses iodate and bisulfite with starch as indicator, and its many variations such as the "Old Nassau" (2) clock reaction, which adds mercuric ion to the Landolt formula, are probably the most popular of all clock reactions. The formaldehyde-bisulfite clock reaction (3), which can be used with a variety of pH indicators, is also popular, while other clock reactions are used much less commonly (4). The continued popularity of the Landolt clock stems from its ease of preparation and use of reagents that are generally available to the high school or college teacher.

We sought an iodine clock reaction that would produce an effect similar to that afforded by the Landolt clock reaction, but which could be performed by a demonstrator without access to a chemistry laboratory or reagents. In particular, for use of the demonstration in public audiences, we wished to employ only consumer-available chemicals that are generally recognized as safe, such as might be purchased at a supermarket and commonly found in the home. Such a reaction would mitigate potential issues surrounding the transportation of chemicals, their use in a public setting, and the disposal of waste. Teachers or demonstrators at the elementary school level could also perform such a reaction. Thus we set out to identify a system that would produce an effect similar to that of the Landolt and Old Nassau reactions without the use of iodate, bisulfite, or mercury compounds. The reaction between hydrogen peroxide and an acidic solution containing potassium iodide and sodium thiosulfate has been known to produce a clock reaction effect (5). Our attention quickly centered on the possibility of using ascorbic acid as the reducing agent in place of sodium bisulfite or thiosulfate. The reaction between iodine and ascorbic acid is both rapid and quantitative; in fact, the standard assay for ascorbic acid is iodometric titration (6). Ascorbic acid reacts with iodine according to the following equation (7):



The oxidation product, a strained and activated lactone, spontaneously hydrolyzes in aqueous solution to afford

L-threo-2,3-hexodiulosonic acid or 4,5,6-trihydroxy-2,3-diketo-hexanoic acid (8):



The by-product of the ascorbic acid oxidation is hydriodic acid, which is readily oxidized to elemental iodine and water by many oxidizing agents, including hydrogen peroxide. Hydrogen peroxide is inexpensive, safe, and readily available. Thus the reaction between hydrogen peroxide and ascorbic acid, mediated by an iodide-iodine electron carrier system, could provide the basis for a clock reaction provided that (i) the direct reaction between hydrogen peroxide and ascorbic acid was relatively slow, and (ii) the kinetics were such that an appropriate time delay could be found using reasonable concentrations of reactants at room temperature. The latter was a particular issue, because hydrogen peroxide is available to the consumer only as a 3% solution,¹ and the necessary iodine is available only as tincture of iodine, sold as a topical disinfectant.²

Experimentation showed that the production of a clock reaction was in fact possible by the use of ascorbic acid, 3% hydrogen peroxide, tincture of iodine, and starch. The time required to reach the iodine-starch endpoint could be adjusted by varying the amount of water used to dilute the reactants. Further experimentation showed that the reaction could be carried out using commercial vitamin C supplement tablets as the source of ascorbic acid. Although these tablets contain some inert and insoluble excipients, the actual amount is relatively small and the presence of the excipients did not adversely affect the use of the tablets.³ No filtration was required when using vitamin C tablets, the tablets simply being finely crushed and dissolved in water. A variation of the reaction was found to be possible using orange juice as the source of ascorbic acid. This resulted in an orange-to-black clock reaction similar to that seen in the Old Nassau variant of the Landolt clock. This modification makes an entertaining Halloween demonstration.

Somewhat greater variability in the time required to reach the endpoint was encountered when using vitamin C tablets. This variability was dependent upon how completely the vitamin C in the tablets was dissolved. As might be an-

Table 1. Results Using Various Liquids to Prepare Solutions A and B

Liquid	Time to Endpoint/s
Water	45–50
pH 2 buffer	45–50
pH 4 buffer	45–50
pH 5 buffer	30–35
pH 6 buffer	20–25
pH 7 buffer	17–22
pH 8 buffer	25–30
pH 9 buffer	No color
White vinegar	45–50

Table 2. Procedure A Results

Solution A			Solution B			Time/ s
Vitamin C Stock/ mL	Tincture of Iodine/ mL	Water/ mL	Hydrogen Peroxide/ mL	Starch Solution mL	Water/ mL	
5	5	120	15	3	120	80–95
5	5	60	15	3	60	40–50
5	5	30	15	3	30	20–25

Table 3. Procedure B Results

Solution A			Solution B			Time/ s
Vitamin C Stock/ mL	Tincture of Iodine/ mL	Water/ mL	Hydrogen Peroxide/ mL	Starch Solution mL	Water/ mL	
5	5	120	15	3	120	50–65
5	5	60	15	3	60	35–50
5	5	30	15	3	30	15–25

anticipated, there was much greater variability in the time required to reach the endpoint when kitchen implements such as measuring cups and spoons were used to measure volumes.

Despite the sensitivity of ascorbic acid to oxidation by various transition metal ions, it was found that the solutions could be prepared with distilled water, deionized water, or tap water. However, some variability in reaction times has been noticed when tap water from different locations was used. Small concentrations of magnesium, calcium, and chloride ions did not appear to cause a significant change in the time required for completion of the reaction. Experimentation suggested that the pH and buffering capacity of the water was the cause. To understand the cause of variability in reaction time when different tap water sources were used, the pH of the reaction mixture was measured and the reaction was conducted in buffer solutions at different pH values.

After the combination of water with the vitamin C stock solution, solution A was found to have a pH of about 4. Upon addition of the tincture of iodine, the pH dropped to about 1.5 as hydriodic acid was formed by reduction of the iodine according to eq 1. The pH of the reaction mixture during the subsequent reaction with hydrogen peroxide did not

change significantly. To study this further, the reactions were carried out using commercial pH buffer solutions in place of water for the preparation of solutions A and B. These results, and a comparison to results obtained with distilled water, are summarized in Table 1. In each case, 60 mL of water or buffer was used to prepare solution A and 60 mL of the same liquid was used to prepare solution B. From these data it will be seen that the reaction becomes faster as the pH approaches neutral. The failure to reach a color change endpoint at pH 9 may be due to the disproportionation of iodine to iodide and hypoiodite that occurs at higher pH. The use of white vinegar instead of distilled water to prepare solutions A and B gave results similar to those obtained using distilled water.

For the most reproducible results, the use of distilled or deionized water is recommended. Tap water or softened water may be used but reproduction of the reaction as published cannot be assured. White vinegar may be used if distilled or deionized water is unavailable and tap water is not acceptable.

Experimental Section

Ascorbic acid (vitamin C) was purchased from Aldrich. Tincture of iodine (USP, 2%), hydrogen peroxide (USP, 3%), vitamin C supplement tablets,⁴ and starch solution⁵ were purchased from a local supermarket and used as purchased. Distilled water was purchased from a local pharmacy. Liquid volumes were measured using Nalgene polypropylene student-grade graduated cylinders. Ascorbic acid (vitamin C) solutions are degraded by aerial oxidation and must be freshly prepared for best results.

Tincture of iodine USP 2%, also known as “mild tincture of iodine”, was used in these experiments. A stronger solution, containing 7% iodine, may be available in some locales and is not suitable for use in this demonstration. A product with a similar name, tincture of iodides, also known as “decolorized iodine”, is sold in some areas and is likewise not suited for this demonstration.

Procedure A. Reaction Using Laboratory Ascorbic Acid

A stock solution of 0.1 M ascorbic acid was prepared by dissolving 1000 mg of ascorbic acid in 60 mL of water. Equal volumes of this stock solution and tincture of iodine were added⁶ into water to afford solution A. Hydrogen peroxide (H_2O_2) and approximately 3 mL of starch solution were added into water to afford solution B.⁷ To perform the reaction, solutions A and B were poured simultaneously into a container and swirled to effect mixing. The rate of the reaction, and thus the time to the color change endpoint, was a function of the volume of water used to prepare solutions A and B. Larger volumes of water led to a longer delay before the color change occurred. Results are summarized in Table 2.

Procedure B. Reaction Using Vitamin C Tablets

The ascorbic acid (vitamin C) stock solution was prepared from vitamin C tablets containing 1000 mg of ascorbic acid in 60 mL of water. The tablets were finely pulverized in the water until no particles remained. This stock solution was combined with tincture of iodine and water to prepare solution A. Starch solution, 3% hydrogen peroxide, and water were combined to prepare solution B as described in Procedure A. Typical results are summarized in Table 3.

Procedure C. Reaction Using Orange Juice

Orange juice was allowed to warm to room temperature before use. Solution A was prepared by the addition of 5 mL of tincture of iodine to 280 mL of orange juice. The mixture was shaken thoroughly until the dark color was discharged, after which 3 mL of starch solution was added. The reaction was started by the addition of 50 mL of 3% hydrogen peroxide and the flask was shaken or stirred to mix the contents again. The color change from orange to black required approximately 35 to 45 seconds.

Procedure D. Reaction Using Kitchen Measuring Ware

If graduated ware is not available, the vitamin C stock solution may be prepared from vitamin C tablets containing 1000 mg of ascorbic acid in 4 tablespoons (60 mL) of water. Solution A is then prepared from 1 teaspoon (5 mL) of the vitamin C stock solution, 1 teaspoon (5 mL) of tincture of iodine, and 2 tablespoons (30 mL) of water. Solution B is prepared from 1 tablespoon (15 mL) of 3% hydrogen peroxide, $\frac{1}{2}$ teaspoon (2.5 mL) of laundry starch, and 2 tablespoons (30 mL) of water. The endpoint is reached in approximately 30 to 45 seconds. As noted earlier, this procedure results in considerably more variability in the delay interval prior to the color change.

A larger-volume demonstration may be arranged by adding 2 fluid ounces (60 mL) of tincture of iodine to the entire quantity (60 mL) of vitamin C stock solution prepared above and diluting with $1\frac{1}{2}$ cups (360 mL) of water to give solution A. Solution B is prepared from $\frac{1}{2}$ cup (180 mL) of 3% hydrogen peroxide, 2 teaspoons (10 mL) of laundry starch, and $1\frac{1}{2}$ cups (360 mL) of water.

Hazards

Elemental iodine is poisonous. Tincture of iodine and the clock reaction mixture must be kept away from children. Before disposal the clock reaction mixture should be reduced by the addition of ascorbic acid (vitamin C) until it is colorless. Tincture of iodine contains 50% ethyl alcohol and is flammable.

Notes

1. This corresponds to approximately 0.9 M hydrogen peroxide.
2. Tincture of iodine 2% USP contains 0.08 M I_2 and 0.16 M sodium iodide in a solution of ethyl alcohol and water. It is prepared by dissolving 20 g of iodine and 24 g of sodium iodide in

500 mL of 95% ethyl alcohol and diluting the mixture to 1 L with water. The checker reports that commercial 7% iodine ("strong tincture of iodine") may be diluted with $2\frac{1}{2}$ times its volume of water to a nominal 2% concentration for use.

3. For example, a 250-mg nonchewable vitamin C tablet was found to have a mass of 295 mg. It contains 250 mg, or 1.4 mmol, of ascorbic acid and 45 mg of excipients.

4. Tablets labeled "chewable" or "flavored" should not be used. They contain much higher quantities of excipients, including sweeteners and flavors, which may interfere with the clock reaction.

5. Linit brand laundry starch was used. A 1% or 0.5% laboratory starch solution may also be used. If starch solution is not available, a satisfactory solution may be prepared by stirring 5 g (1 to 2 tsp) of cornstarch with 30 mL (2 tbsp) of cold water until a uniform thin suspension is formed. This suspension is poured slowly into 500 mL (2 cups) of *vigorously* boiling water with stirring so that the boiling does *not stop*. The solution is allowed to cool before use.

6. Combining equal volumes of the ascorbic acid stock solution and tincture of iodine, without additional dilution, gives a mixture containing 0.005 M ascorbic acid and 0.16 M iodide.

7. It is not important that the starch solution be measured precisely.

Literature Cited

1. See, for example: Shakhshiri, B. Z. *Chemical Demonstrations*, Vol. 4; University of Wisconsin Press: Madison, WI, 1992; pp 16–25 and references cited therein. *Tested Demonstrations in Chemistry*; Alyea, H. N.; Dutton, F. B., Eds.; Journal of Chemical Education: Easton, PA, 1965; pp 19, 85. Ford, L. A.; Grundmeier, E. W. *Chemical Magic*, 2nd ed.; Dover: New York, 1993; p 102.
2. See, for example: Shakhshiri, B. Z. Op. cit.; pp 29–36 and references cited therein. Alyea, H. N.; Dutton, F. B. Op. cit.; p 19.
3. See, for example: Shakhshiri, B. Z. Op. cit.; pp 70–74 and references cited therein. Alyea, H. N.; Dutton, F. B. Op. cit.; p 85.
4. For example, the base-catalyzed condensation reaction between acetone and cinnamaldehyde affords a precipitate of cinnamylacetone; see: Alyea, H. N.; Dutton, F. B. Op. cit.; p 220.
5. See, for example: Shakhshiri, B. Z. Op. cit.; pp 43–74 and references cited therein. Alyea, H. N.; Dutton, F. B. Op. cit.; p 85.
6. *The United States Pharmacopeia USP 24*; National Publishing: Philadelphia, PA, 1999; p 160.
7. Kenyon, J.; Munro, N. J. *Chem. Soc.* **1948**, 158–161.
8. This substance has been identified as the phenylhydrazone derivative; see: Rao, J. M.; Nair, P. M. *Tetrahedron* **1970**, *26*, 3833–3838.