The Titrimetric Analysis of Vitamin C in Dietary Supplements

Topics for Study: Oxidation numbers, Oxidation-Reduction Reactions

Technical and Theoretical Skills

In this assignment you will

- use an analytical balance
- make a standard solution
- use a volumetric pipet
- make a volumetric solution
- perform a redox titration
- determine the composition of a commercial vitamin C tablet

Safety Precaution

Dispose of the remaining potassium iodate solution (KIO_3) in the "Waste oxidants" container and the $Na_2S_2O_3$ solution in the "Waste Reducing agent" container.

Introduction

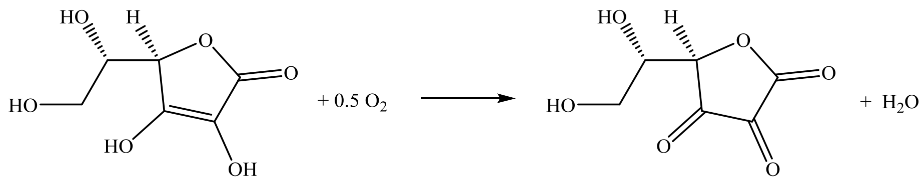
There are two parts to this experiment. In the first part, you will prepare a primary standard potassium iodate solution (KIO_3) and use it to standardize a sodium thiosulfate solution. In the second part, you will determine the amount of vitamin C in a vitamin C tablet by titration using your standard sodium thiosulfate solution.

Background

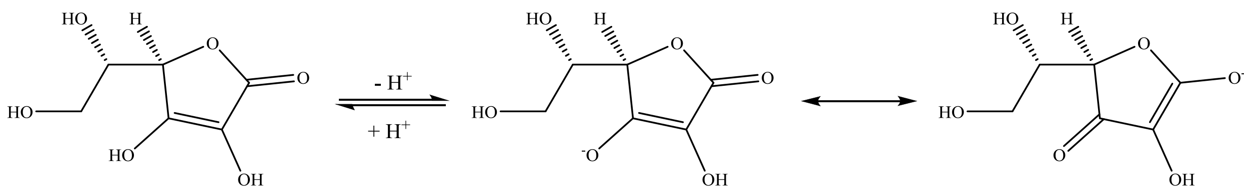
The human body does not synthesize vitamins.Therefore, the vitamins that we need for catalyzing specific biochemical reactions must be acquired through the food that we eat. Vitamin C (ascorbic acid) is found in many fruits and vegetables, particularly in citrus fruit juices. It is also one of the more popular additives in modern food-processing technology since it prevents the enzymatic browning that frequently occurs with cut fruits and vegetables. Storage and processing, however, causes vegetables to lose a part of their vitamin C content. Boiling or steaming extracts the water-soluble vitamin C from the vegetables and high temperature accelerates its degradation by air oxidation. Thus, eating raw, freshly harvested fruits and vegetables maximize your intake of vitamin C. The accepted recommended daily intake is 60 mg for adults. However, several scientist (i.e., Linus Pauling) proposed significantly higher doses (>1000 mg) to cure cancer and fight heart disease.

Long before the structure was elucidated, the therapeutic ability of vitamin C to prevent scurvy was known. In 1775, the British explorer Captain James Cook required that all his sailors be issued rations of lime juice. His three-year, extensive exploration of the South Pacific was equally notable for the health that his crew maintained. To this day, the slang term "limey" referring to a British person derives from this common use of lime juice for the British merchant fleet during the dominance of the seas by Britain during the 19th century.

Vitamin C (compound I) is a colorless, water-soluble acid ($K_a = 6.7 \times 10^{-5}$, one of the enolic protons is lost) and also a powerful biochemical reducing agent that readily undergoes air oxidation to dehydroascorbic acid (II).

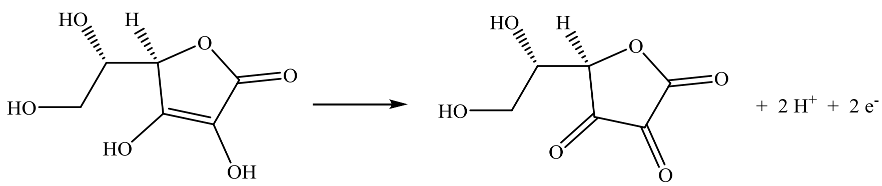


(I) **(II)**



Redox Reactions

Half reactions do not occur by themselves. Electrons are too reactive to sit around for long. For every oxidation there will be a reduction because the electrons released in the oxidation reaction have to be used up elsewhere. The direction of the spontaneous reaction is governed by the difference in the electrode potential of the half reactions. The system will always move spontaneously in the direction to lower free energy. The spontaneous reaction that you will study in this assignment involves the following two half reactions.



$$3\,I^- \longrightarrow I_3^- + 2\,e^-$$

Since both reactions involve two electrons, the stoichiometry between ascorbic acid and triiodide ion (or I_2) is 1:1.

Iodine is a widely used mild oxidizing agent, but due to its volatility, it is difficult to work with standard solutions of this reagent. Some stabilization and an enhanced solubility can be achieved by preparing aqueous solutions of I_2 in an excess of iodide (I^-); the iodine then exists predominantly as the triiodide ion, I_3^-.

$$I_2 + I^- \leftrightarrows I_3^-$$

In the part I of this experiment, you will prepare a solution of potassium iodate, which can oxidize I^- to I_2, and use it to standardize a sodium thiosulfate solution. The standard sodium thiosulfate solution is subsequently used for a titrimetric redox analysis of excess I_3^- in part II.

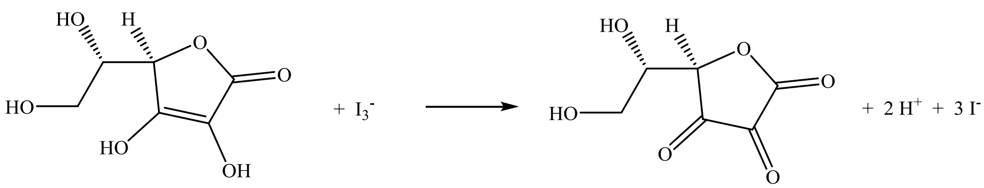
The unknown sample, whether it is the amount of sodium thiosulfate in the solution or an vitamin C in tablet is treated with a measured amount of iodate ion, IO_3^-, in an acidic solution containing an excess of I^-. The red-brown triiodide ion, I_3^-, a milder oxidizing agent than IO_3^-, forms in solution (Eq. 1):

$$IO_3^-{}_{(aq)} + 8\ I^-{}_{(aq)} + 6\ H^+{}_{(aq)} \longrightarrow 3\ I_3^-{}_{(aq)} + 3\ H_2O_{(l)} \qquad \text{(Eq. 1)}$$

The chemical analysis for the standardization of the sodium thiosulfate solution is summarized in the net ionic equation, (Eq. 2).

$$IO_3^-{}_{(aq)} + 6\ S_2O_3^{2-}{}_{(aq)} + 6\ H^+{}_{(aq)} \longrightarrow I^-{}_{(aq)} + 3\ S_4O_6^{2-}{}_{(aq)} + 3\ H_2O_{(l)} \qquad \text{(Eq. 2)}$$

Once the triiodide ion forms in (Eq. 1) it reacts with any ascorbic acid in solution to form dehydroascorbic acid (Eq. 3)



(Eq. 3a)

Or when written in a condensed formula notation:

$$C_6H_8O_{6(aq)} + I_3^-{}_{(aq)} \longrightarrow C_6H_6O_{6(aq)} + 3\ I^-{}_{(aq)} + 2\ H^+{}_{(aq)} \qquad \text{(Eq. 3b)}$$

The excess I_3^- is titrated with standard thiosulfate, $S_2O_3^{2-}$, solution producing colorless I^- and $S_4O_6^{2-}$ ions (Eq. 4)

$$2\ S_2O_3^{2-}{}_{(aq)} + \underset{\text{excess}}{I_3^-{}_{(aq)}} \longrightarrow 3\ I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)} \qquad \text{(Eq. 4)}$$

The difference in the amount of the I_3^- generated from the IO_3^- in Eq. 1 and the amount in excess that is titrated in (Eq. 4) is a measure of the ascorbic acid content of the sample.

The end point of the titration can be determined by adding a quantity of starch solution to serve as an indicator just prior to the disappearance of the red-brown I_3^- in the titration. Starch forms a tightly bound, deep blue ion with triiodide, $[I_3\bullet\text{starch}]^-$, (Eq. 5).

$$3\ I_3^-{}_{(aq)} + 3\ \text{starch}_{(aq)} \longrightarrow 3\ [I_3\bullet\text{starch}]^-{}_{(aq,\ deep\text{-}blue)} \qquad \text{(Eq. 5)}$$

The addition of the $S_2O_3^{2-}$ titrant is continued until the $[I_3\bullet\text{starch}]^-$ is reduced to I^-, the solution appears colorless at the end point, (Eq. 6)

$$3\ [I_3\bullet\text{starch}]^- + 6\ S_2O_3^{2-}{}_{(aq)} \longrightarrow 9\ I^-{}_{(aq)} + 3\ S_4O_6^{2-}{}_{(aq)} + 3\ \text{starch}_{(aq)} \qquad \text{(Eq. 6)}$$

EXPERIMENTAL

Preparation of a 5 % Starch Solution: Weigh approximately 1 g of soluble starch on the balance. Set aside. Bring 15 mL of water to a gentle boil in a 50-mL Erlenmeyer flask. While the water is heating, prepare slurry of the starch in 5 mL of cold water in a small beaker. Slowly pour the slurry into the boiling water with stirring. Set aside to cool.

Preparation of a Standard Potassium Iodate Solution: Using the analytical balance precisely measure about 0.5 g of KIO_3 to the nearest tenth of a milligram. Transfer the solid to a 250-mL volumetric flask. Dissolve the solid using about 150 mL of distilled water and then dilute the solution to the mark with distilled water. Record the weight in your notebook in order to calculate the molar concentration of the KIO_3 solution.

Standardization of a Sodium Thiosulfate Solution: Transfer about 100 mL of stock $Na_2S_2O_3$ solution to a clean but not necessarily dry Erlenmeyer flask. Prepare a clean, 25-mL burette for titration. Rinse it and fill with the stock $Na_2S_2O_3$ solution. Read and record the volume. Pipet 20 mL of the standard KIO_3 solution into a 125-mL Erlenmeyer flask and add about 1 g of solid KI. Add about 0.1 g of $NaHCO_3$ and 10 mL of 0.2 M H_2SO_4. **The weights of the KI and $NaHCO_3$ do not need to be known precisely.**

Immediately begin titrating with the $Na_2S_2O_3$ solution. When the red-brown solution (due to I_3^-) changes to a pale yellow color, add about 10 drops of starch solution. Stirring constantly and continue titrating slowly until the blue color disappears.

Repeat the titration twice. In these subsequent titrations, rapidly add the $Na_2S_2O_3$ titrant until 1 mL before the expected endpoint. Add the starch solution and continue titrating drop wise until the solution is colorless. Repeated analyses should be within ±1 %.

Prepare again 5 % starch solution during second lab period. Starch solution has to be fresh.

Vitamin C Sample Preparation: Using an analytical balance, weigh a vitamin C "tablet" and place it in a mortar. Grind with a pestle into fine powder. Weigh approximately 0.10 g of the powder to a tenth of a milligram and transfer it quantitatively into a 125-mL Erlenmeyer flask. Record the weight in your notebook. Dissolve the powder in 15 mL of distilled water.

Titrimetric Analysis of Vitamin C: Using your 10-mL pipet, transfer 30 mL of standard KIO_3 solution into the sample solution above and then add approximately 1 g of solid KI, 10 mL 0.2 M H_2SO_4, and 0.1 g of $NaHCO_3$ to the flask.

Titrate the excess I_3^- in the sample with your standardized $Na_2S_2O_3$ solution. After the red-brown solution changes to a faint, pale yellow color, add about 10 drops of starch solution. Stirring constantly, continue titrating slowly until the blue color disappears. Be sure to wait about 30 seconds after the color disappears to ensure completion otherwise add a few drops of the $Na_2S_2O_3$ solution.

Read and record the final burette reading. Repeat the analysis twice in order to complete three trials. The relative average deviation of the titrant volumes should be less than ±1 %.

All solution of KIO_3 and $Na_2S_2O_3$ may be safely disposed in the sink.