

COLORFUL CATALYSIS: THE OXIDATION OF TARTARIC ACID BY HYDROGEN PEROXIDE WITH A COBALT CHLORIDE CATALYST

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Solutions needed:

Potassium sodium tartrate (Rochelle Salt), 0.3 M: Dissolve 84.6 grams of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4 \text{H}_2\text{O}$ in water to make 1 liter of solution.

6% hydrogen peroxide: Dilute 100 mL 30% H_2O_2 to 500 mL
(Note: 6% H_2O_2 is available commercially as "20 volume" hydrogen peroxide for use in bleaching hair.)

Cobalt(II) chloride, 0.3 M : Dissolve 10 grams of CoCl_2 in water to make 250 mL solution.

Procedure:

Prepare five beakers, one will be a control: use 600-mL beakers

Add to each beaker: 200 mL potassium sodium tartrate solution
 65 mL 6% H_2O_2 solution
 (NOTE: Use a 3:1 ratio of tartrate to peroxide)

Cover the beakers with watch glasses and heat 4 of them on a hot plate. Remove one beaker when the temperature is about 45°C (Try to maintain the temperature in this beaker at 45°C while continuing to heat the others.)

Remove the second beaker from the heat when the temperature is about 55°C .

Remove the remaining two beakers from the heat when the temperature is about 65 - 70°C .

Line up four beakers of solution: the one at room temperature, the one at 45°C, the one at 55°C and one of the beakers at 65 - 70°C. Keep the second beaker at 65 -70°C as a control to show that the uncatalyzed reaction proceeds slowly.

Add 15 mL of the CoCl_2 solution simultaneously to each of the four beakers. Cover and observe.
(NOTE: The reaction is vigorous and it may overflow. If this happens, reduce the amount of solution used for future demonstrations, or use larger beakers.)

After reaction is complete, pour a small amount of the spent solution from one of the beakers into the control (the fifth beaker which had been heated to 65 -70°C) cover and observe.

If desired, additional beakers of solution can be prepared at various temperatures, from room temperature to 65-70°C, and a small amount of spent solution from the above reactions can be poured into the solutions in each beaker, cover and observe. Also, if a series of solutions are used, some of this spent solution can be poured into one beaker, and then, after the reaction has subsided, some of that spent solution poured into the next beaker, etc.

Utilization:

Catalysis. Using any solution, as listed in the preceding section, with a control, shows the effect of a catalyst on the rate of reaction. Without the catalyst, the rate of reaction, as evidenced by the evolution of CO₂ gas (or lack of evolution of CO₂ gas), is very slow.

Activated complex. This demonstration clearly shows the role of an activated complex in a reaction mechanism. Initially, the catalyst, CoCl₂, is pink, but when added to the reaction mixture, a green complex is formed and the reaction becomes most vigorous. As the tartrate is oxidized, the catalyst will be regenerated and the solution will return to a pink color.

Regeneration of the catalyst. By taking some of the spent reaction mixture and adding it to a fresh tartrate-peroxide mixture, the entire reaction sequence will be repeated, complete with the green activated complex. This shows that the original catalyst was regenerated at the end of the reaction and is still available to catalyze another reaction.

The effect of temperature. By direct comparison of the reaction at various temperatures (25°, 45°, 55° and 65°), the effect of temperature on reaction rate can clearly be observed. If desired, the reaction can be timed. Start the timer when the catalyst is added and stop it when the pink color of the catalyst is regenerated. (NOTE: At temperatures above 70°C the reaction is very vigorous and will foam over the sides of the reaction container.)

A Hypothetical Mechanism

The green activated complex is a result of a superoxide linkage between two octahedral coordinated cobalt atoms. (See Figure 1) In the presence of the hydrogen peroxide, the Co atoms are linked by a peroxo linkage which oxidizes to a superoxo complex. (Note: peroxo complexes of cobalt are usually brown in color and the superoxo linkages are known to be green.) The unpaired electrons belonging to the O₂⁻ resides in a molecular orbital of π symmetry relative to the planar Co-O-O-Co grouping and is delocalized over these four atoms. The Co atoms are formally described as Co(III) ions. (See Figure 2)

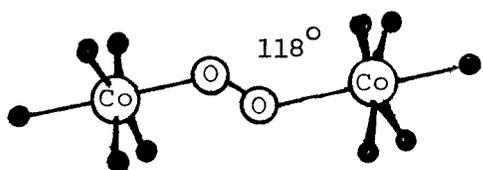


Figure 1. The cobalt complex

The O-O bond length is 131 pm

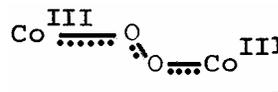


Figure 2. The superoxo linkage showing delocalized electrons

The tartaric acid molecules coordinate about the cobalt complex possibly like that shown below. This is based on the fact that there are a number of compounds that bridge cobalt in octahedral cobalt complexes. An example is acetylacetonate (or 2,4-pentanedione) which is similar in structure to tartaric acid. This would provide a better symmetry for oxidation of the middle carbons of the tartaric acid to CO₂ and the hydrogens to H₂O. As the reaction goes to completion, the superoxide linkage breaks and the oxygens are replaced by Cl⁻ ions.

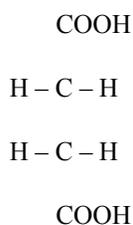


Figure 3. Tartaric acid

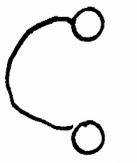


Figure 4. Tartaric acid schematic representation

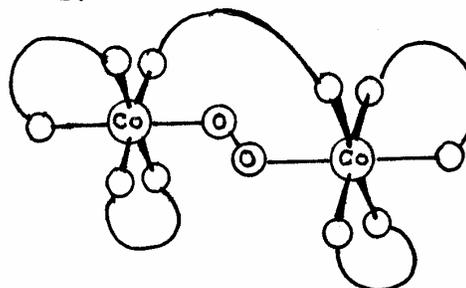


Figure 5. Schematic representation of the cobalt-tartaric acid complex

Reference:

This procedure is based on:

Ruda, Paul T., **J. Chem Ed.**, **55** (10), 652, (Oct. 1978)

The mechanism is based on personal experiments and information from:

Cotton, F. A. and G. Wilkinson, **Advanced Inorganic Chemistry**, 5th Ed., Wiley, 1988, pages 468-470, 727-728, and 735-737

Greenwood, N. N. and A. Earnshaw, **Chemistry of the Elements**, Pergamon Press, 1984, pages 719-722, 1306-1307, and 1311-1312