Advanced Inorganic Chemistry Andy Aspaas & Levi Stanley
Demonstration Summary 12/4/2000

The Belousov-Zhabotinski Reaction

Although more difficult to perfect than the Briggs-Rauscher reaction, the Belousov-Zhabotinski reaction is an extremely striking demonstration, visually. It so turns out that the reaction is chemically striking as well. It was discovered by Russian chemist Boris P. Belousov in the 1950s. This reaction came about from Belousov's attempts to find an inorganic analog to the Krebs cycle. His work was submitted to eastern journals, but was rejected on the grounds that "it's impossible." Devastated by this rejection, Belousov decided to leave science forever. Biochemistry professor S.E. Schnoll urged Belousov to continue his work, but to no avail. Belousov was content to simply hand the recipe to Schnoll. This led to A.M. Zhabotinski's elucidation of the mechanism and spatial distribution patterns of the reaction, under the direction of Schnoll.

In this reaction, three solutions are mixed to form a green color, which turns blue, purple, and red, and then cycles back to green and repeats. This reaction involves the following three solutions: solution A is 0.23M $KBrO_3$, solution B is 0.31M malonic acid and 0.059M KBr, and solution C is 0.019M cerium(IV) ammonium nitrate and 2.7M H_2SO_4. During presentation, a small amount of the indicator ferroin is spiked into the solution. In the original reaction, Belousov used citric acid in the place of malonic acid. It was later determined that a number of carboxylic acids could be used. Also, manganese ions could be used instead of cerium.

The overall B-Z reaction is the cerium-catalyzed oxidation of malonic acid by bromate ions in dilute sulfuric acid. This reaction is represented by the following

$3\ CH_2(CO_2H)_2 + 4\ BrO_3^- \rightarrow 4\ Br^- + 9\ CO_2 + 6\ H_2O$ (1)

The mechanism for this reaction involves two processes. Process A involes ions and two-electron transfers, while process B involves radicals and one-electron transfers. The concentration of bromide ions determines which process is dominant. Process A is dominant when bromide ion concentration is high, while process B is dominant when bromide ion concentration is low.

Process A is the reduction of bromate ions by bromide ions in two electron transfers. It can be represented by this net reaction:

$BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$ (2)

This occurs when solutions A and B are mixed. This process occurs through the following three steps:

$BrO_3^- + Br^- + 2\ H^+ \rightarrow HBrO_2 + HOBr$ (3)
$HBrO_2 + Br^- + H^+ \rightarrow 2\ HOBr$ (4)
$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$ (5)

The bromine created from reaction 5 reacts with malonic acid as it slowly enolizes, as represented by the following equation:

$Br_2 + CH_2(CO_2H)_2 \rightarrow BrCH(CO_2H)_2 + Br^- + H^+$ (6)

These reactions function to reduce the concentration of bromide ions in the solution. This allows process B to become dominant.

The overall reaction of process B is represented by the following equation:

$2\ BrO_3^- + 12\ H^+ + 10\ Ce^{3+} \rightarrow Br_2 + 6\ H_2O\ 10\ Ce^{4+}$ (7)

and is composed of the following steps:

$BrO_3^- + HBrO_2 + H^+ \rightarrow 2\ BrO_2\bullet + H_2O$ (8)
$BrO_2\bullet + Ce^{3+} + H^+ \rightarrow HBrO_2 + Ce^{4+}$ (9)
$2\ HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$ (10)
$2\ HOBr \rightarrow HBrO_2 + Br^- + H^+$ (11)

$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$ (12)

Key elements to this sequence include the net result of equation 8 plus twice equation 9, which is shown below:

$2\ Ce^{3+} + BrO_3^- + HBrO_2 + 3\ H^+ \rightarrow 2\ Ce^{4+} + H_2O + 2HBrO_2$ (13)

This sequence produces bromous acid autocatalytically . Autocatalysis is an essential feature of this reaction, but does not continue until the reactants are depleted, because there is a 2nd-order destruction of $HBrO_2$, as seen in reaction 10. Reactions 11 and 12 represent the disproportionation of hyperbromous acid to bromous acid and Br_2. Cerium(IV) ions and bromine oxidize malonic acid to form bromide ions. This causes an increase in bromide ion concentration, which reactivates process A.

The colors in this reaction are formed mainly by the oxidation and reduction of iron and cerium complexes. Ferroin provides two of the colors seen in this reaction: as [Ce(IV)] increases, it oxidizes the iron in ferroin from red iron(II) to blue iron(III). Cerium(III) is colorless and cerium(IV) is yellow. The combination of cerium(IV) and iron(III) makes the green color. Under the right conditions, this cycle will repeat several times. Cleanliness of glassware is a concern because the oscillations are interrupted by chloride ion contamination.

Questions:

1. If the Briggs-Rauscher and the BZ reactions both consist of two complimentary processes, why are 4 colors visible in the BZ reaction and only 2 in the Briggs-Rauscher reaction?

   Answer: The Briggs-Rauscher reaction involves complexes with iodine and starch to give the main color change. The BZ reaction involves the oxidation and reduction of two transition metal complexes: iron and cerium. The green color arises from the combination of yellow cerium(IV) and blue iron(III). The purple color comes about when there are equal concentrations of iron(III) and iron(II).

2. What is autocatalysis, and how does it apply to this reaction:

   Answer: A process is autocatalytic when it produces its own catalyst in the reaction sequence. The combination of equations 8 and 9 consume and replenish bromous acid equally.

3. Name a species that could be successfully used in place of the following reactants: cerium, malonic acid.

   Answer: manganese could be used in place of cerium, and citric acid or a number of other carboxylic acids could be used in place of malonic acid.

References:

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