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Detailed Reaction Mechanism

The overall reaction involves the production of HOI, hypoiodous acid, as an intermediate, as shown below.

$$IO_3^-(aq) + 2H_2O_2(aq) + H^+(aq) \rightarrow HOI(aq) + 2O_2(g) + 2H_2O(l) \quad (1)$$

$$HOI(aq) + CH_2(CO_2H)_2(aq) \rightarrow ICH(CO_2H)(aq) + H_2O(l) \quad (2)$$

In reaction 1, iodate is reduced by peroxide. There are two competing mechanisms for this reaction: a radical mechanism, 1a, and a non-radical one, 1b.

1a — Radical Mechanism

i. $2IO_3^- + 2HIO_2 + 2H^+ \rightarrow 4IO_2\bullet + 2H_2O$

ii. $4IO_2\bullet + 4Mn^{2+} + 4H_2O \rightarrow 4HIO_2 + 4Mn(OH)^{2+}$

iii. $4Mn(OH)^{2+} + 4H_2O_2 \rightarrow 4Mn^{2+} + 4H_2O + 4HOO\bullet$

iv. $4HOO\bullet \rightarrow 2H_2O_2 + 2O_2$

v. $2HIO_2 \rightarrow IO_3^- + HOI + H^+$

1b — Non-radical Mechanism

i. $IO_3^- + I^- + 2H^+ \rightarrow HIO_2 + HOI$

ii. $HIO_2 + I^- + H^+ \rightarrow 2HOI$

iii. $2HOI + 2H_2O_2 \rightarrow 2I^- + 2O_2 + 2H^+ + 2H_2O$

Reaction 2 takes place by a two-step reaction sequence.

Reaction 2 Mechanism

i. $I^- + HOI + H^+ \rightarrow I_2 + H_2O$

ii. $I_2 + CH_2(CO_2H)_2 \rightarrow ICH(CO_2H)_2 + H^+ + I^-$

When the reactants are mixed, IO_3^- reacts with H_2O_2 to produce a little HIO_2. Once HIO_2, iodous acid. appears, the radical mechanism, 1a, begins. Steps i, ii, and v are fast, resulting in rapid production of hydroiodous acid, HOI. Since reaction 1a is faster than reaction 2 and $[I^-]$ is low, [HOI] builds up. ❶ HOI can now trigger the production of I^- and I_2 (see Figure 1).

HOI is reduced by H_2O_2, (reaction iii of 1b), to produce I^-. As $[I^-]$ is produced, ❷, HOI reacts with I^-, (reaction i of 2), to form I_2. At this point, the solution is still colorless, since I_2 concentration is still low.

As HOI concentration falls, I^- and I_2 concentrations continue to increase. $[I_2]$ rises first, turning the solution yellow. As $[I^-]$ increases, its reaction rate with HIO_2, (ii of 1b) exceeds the rate for radical steps i and ii and the radical process shuts off. Now $[I^-]$ and $[I_2]$ are high and the solution turns blue, ❸ as I^- and I_2 form a complex with starch.

The non-radical process, along with the second step of reaction 2, depletes both I_2 and HOI. As $[I^-]$ builds up, the solution turns colorless. ❹ At low levels of I_2 and HOI, I^- is consumed in steps i and ii of 1b.

At low $[I^-]$, the rate for steps i and ii of the radical reaction mechanism exceed that for step i of the non-radical one and the radical mechanism takes over. ❺ The process repeats itself and the oscillations continue until either malonic acid or iodate is consumed.

For a more complete discussion of the reaction mechanism, see Shakhashiri and the references therein.

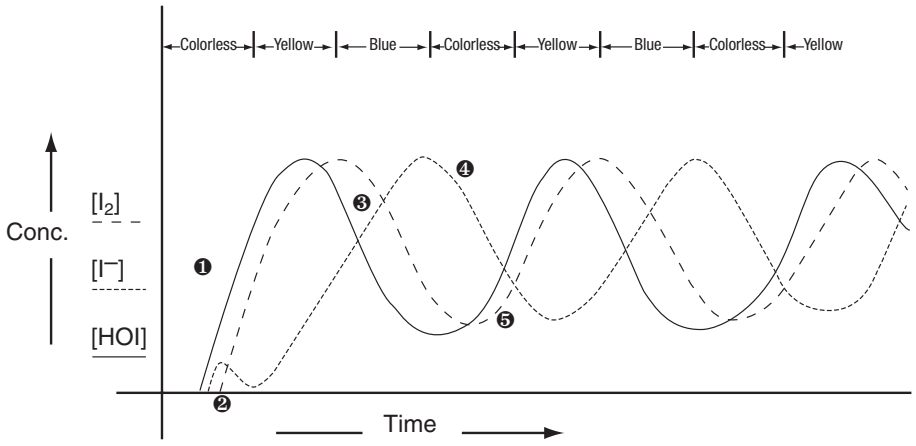

Figure 1.