

A Kinetics Experiment To Demonstrate the Role of a Catalyst in a Chemical Reaction

A Versatile Exercise for General or Physical Chemistry Students

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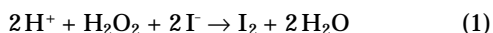
Motivation

Most general and physical chemistry texts explain that a catalyst significantly speeds up a chemical reaction by lowering the activation energy of the reaction (typically by providing an alternate pathway from reactants to products) (1–3). Although this statement seems reasonable, students rarely have a chance to experimentally test its validity. We find that by modifying the common iodine clock reaction, students can use the initial rate method to observe the role of a catalyst in a chemical reaction via activation energy calculations, and evaluate a proposed mechanism. Furthermore, they can determine the order with respect to each reactant and the rate constants of the noncatalyzed and catalyzed (independent of the noncatalyzed) reactions.

Clearly this experiment can be tailored to a general, “advanced” general, or physical chemistry course by altering the number of calculations performed. In addition, the common reagents and equipment required for this experiment render it plausible for institutions operating under strict budget constraints. Perhaps more importantly, our students seem to appreciate the amount of information that can be gleaned from so few experimental steps and they enjoy the dramatic change of each reaction solution from colorless to blue.

Background

The modified iodine clock reaction



can be used to study the concepts described above. For many years, our students have investigated this reaction with a goal of simply defining the order of the reaction and the value of k_{obs} in a buffer solution at pH 4.2. Under these conditions, the rate law takes the form

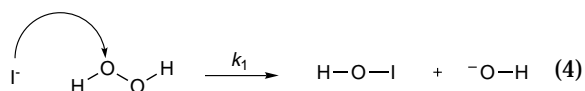
$$\text{rate} = k_{\text{obs}} [\text{H}_2\text{O}_2] [\text{I}^-] \quad (2)$$

However, we have recently run this reaction in our upper-level freshman course and have investigated the acid dependence of k_{obs} . By performing the reaction in the presence of various concentrations of nitric acid, students can determine that this reaction is governed by the two-term rate law

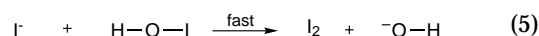
$$\text{rate} = k_{\text{noncat}} [\text{H}_2\text{O}_2] [\text{I}^-] + k_{\text{cat}} [\text{H}^+] [\text{H}_2\text{O}_2] [\text{I}^-] \quad (3)$$

A plot of k_{obs} versus $[\text{H}^+]$ proves to be linear, the slope giving a specific rate constant, k_{cat} , greater than that of the intercept, k_{noncat} , indicating the acid is acting as a catalyst.

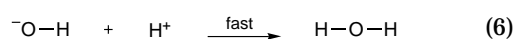
Edwards has clearly described the mechanism of this reaction (4). The first term in eq 3 is a result of a rate-determining nucleophilic attack of I^- upon the H_2O_2 as follows:



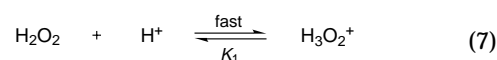
This leads to the formation of I_2 :



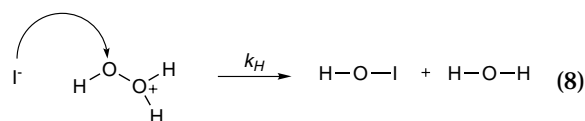
followed by



Whereas the second term in eq 3 results from a fast equilibrium step



followed by



Most students can see that water, being less basic, is a better leaving group than the OH^- and hence the reaction between I^- and H_3O_2^+ should be more favorable. They can also see that k_{cat} is in fact equal to $K_1 k_H$ and that the catalyzed mechanism need not be termolecular.

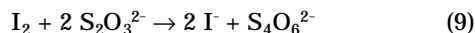
The students repeat the same series of reactions at a low temperature to obtain values of k_{noncat} and k_{cat} at 1 °C. Now that the rate constants at two different temperatures are known, one can calculate the activation energies (E_a) for the catalyzed and noncatalyzed reactions. Typically, they report values of 57 kJ/mol and 42 kJ/mol for the noncatalyzed and catalyzed reactions, respectively. It is encouraging that these values compare favorably to the literature values of 56 kJ/mol and 44 kJ/mol for these reactions (5).

However, it should be pointed out that since $k_{\text{cat}} = K_1 k_H$, it is the values of k_H that one should use in the Arrhenius equation to obtain a true value of E_a of the catalyzed reaction. By using k_{cat} alone, one neglects the temperature dependence of K_1 . Fortunately, the value of K_1 for eq 7 is known to be 2.0×10^{-5} at 25 °C and ΔH for the reaction is +18 kJ/mol (4, 6). Using these values, one calculates K_1 at 1 °C to be 1.0×10^{-5} . Now the Arrhenius equation can be used to calculate E_a for the true acid-catalyzed step (eq 8). Most students arrive at a value of 22 kJ/mol—considerably lower than the 57 kJ/mol obtained for the noncatalyzed reaction (eq 4).

We have found that these additions to an established experiment can lead to a greater understanding of the role kinetics can play in determining the mechanisms of reactions. Also, students clearly see the effect of a catalyst upon a reaction through alteration of the activation energy.

Methods

For each reaction mixture studied, the initial reaction rate will be determined by adding starch and a small known quantity of sodium thiosulfate to the iodide ion solution, before adding hydrogen peroxide. Upon mixing the hydrogen peroxide with the iodide ion, the molecular iodine first produced by eq 1 is immediately consumed by the thiosulfate according to the reaction



However, after the small quantity of thiosulfate is exhausted, the iodine will complex with the starch, changing the color of the reaction solution to dark blue. The interval between final reagent mixing and the color change provides the time data for the mixture.

Stock Solutions

Since the rate of reaction of hydrogen peroxide with iodide ion is greatly influenced by small amounts of contaminants, extreme care must be taken to insure the cleanliness of all glassware. Using tap water, thoroughly wash all glassware, rinse several times with small quantities of distilled water, and drain thoroughly. Small amounts of EDTA can also be added to reduce transition metal effects (7).

It is especially important to accurately deliver (via a 25-mL pipet) the $\text{Na}_2\text{S}_2\text{O}_3$ solution and the stock solutions containing this reagent. However, as the concentrations of all other reagents are in excess, a 25-mL graduated cylinder will provide sufficient measuring accuracy for those species.

Into a 500-mL Erlenmeyer flask, pipet 25 mL of 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$, 25 mL of buffer (1 M $\text{HC}_2\text{H}_3\text{O}_2$ and 1 M $\text{NaC}_2\text{H}_3\text{O}_2$, pH 4.2), and 25 mL of a 2% starch solution. Then dilute by adding 175 mL of distilled water. Swirl the resulting solution to be certain it is homogenous. This buffered stock solution will be used in the noncatalyzed reactions. In a second 500-mL flask, prepare a solution as above but replace the buffer component with 25 additional milliliters of distilled water. This unbuffered stock solution will be used in the acid-catalyzed reactions.

Noncatalyzed Reactions

Into each of five 250-mL Erlenmeyer flasks, pipet 25 mL of the buffered stock solution. To the appropriately numbered flasks, add the quantities of 0.060 M KI solution and distilled water indicated in Table 1. To begin each reaction, quickly add the volume of 0.040 M H_2O_2 solution indicated in the table and note the time. Swirl the reaction flask and record, to the nearest second, the time required for the solution to acquire a blue color. Repeat this procedure for each of the noncatalyzed reactions outlined in Table 1.

Acid-Catalyzed Reactions

To perform the acid-catalyzed reactions, pipet 25 mL of the unbuffered stock solution into each of four 250-mL Erlenmeyer flasks. Follow the remainder of the procedure described above, noting that the required acid solution volumes are also found in Table 1.

Activation Energy Determination

Activation energies are determined by repeating several of the catalyzed reactions at a temperature around 1 °C. To do this, the flask containing the buffered stock solution, the KI, and the distilled water amounts listed in Table 1 should be allowed to stand in an ice bath along with a flask containing some of the H_2O_2 solution and one containing some of the HNO_3 solution. After 30 min, the temperature of these solutions should be recorded. Add the appropriate

Table 1. Reagents Used in Reaction Mixtures

| Flask # | KI 0.060 M (mL) | Distilled H_2O (mL) | H_2O_2 0.040 M (mL) | HNO_3 0.50 M (mL) |
|------------------------------------|-----------------------|---|---|----------------------------------|
| <i>Noncatalyzed</i> | | | | |
| 1 | 25 | 30 | 20 | 0 |
| 2 | 25 | 20 | 30 | 0 |
| 3 | 25 | 0 | 50 | 0 |
| 4 | 15 | 10 | 50 | 0 |
| 5 | 10 | 15 | 50 | 0 |
| <i>Catalyzed</i> | | | | |
| 6 | 25 | 0 | 20 | 30 |
| 7 | 25 | 10 | 20 | 20 |
| 8 | 25 | 20 | 20 | 10 |
| 9 | 25 | 25 | 20 | 5 |
| <i>Catalyzed (low temperature)</i> | | | | |
| 10 | 25 | 0 | 20 | 30 |
| 11 | 25 | 10 | 20 | 20 |
| 12 | 25 | 20 | 20 | 10 |
| 13 | 25 | 25 | 20 | 5 |

amount of HNO_3 followed by H_2O_2 to each reaction flask (keeping it in the ice bath), swirl, and record the time required for the blue color to appear. Repeat for each solution described in the table.

Calculations

As mentioned previously, this experiment can be tailored to suit the needs of several different chemistry courses. Ideally, students employ a computer spreadsheet to perform the calculations outlined below. Suggested column headings and some sample data are presented in Tables 2 and 3.

Rate Law and Reaction Order in H_2O_2 and I^- of the Noncatalyzed Reaction

Using the quantity of thiosulfate ion present in each reaction mixture (2.5×10^{-4} M) and eq 9, calculate the concen-

Table 3. Sample Data from the Catalyzed Reactions

| Flask # | $[\text{H}^+]$ (M) | Time (s) | Rate of I_2 Formation (M/s) | k_{obs} ($\text{M}^{-1}\text{s}^{-1}$) |
|---|-----------------------|-------------|--|--|
| <i>T</i> = 24.8 °C | | | | |
| 6 | 0.15 | 29 | 4.4×10^{-6} | 3.7×10^{-2} |
| 7 | 0.10 | 36 | 3.5×10^{-6} | 2.9×10^{-2} |
| 8 | 0.050 | 52 | 2.4×10^{-6} | 2.0×10^{-2} |
| 9 | 0.025 | 70 | 1.8×10^{-6} | 1.5×10^{-2} |
| Statistics: ^a slope = 1.7×10^{-1} ; y-intercept = 1.1×10^{-2} ; r^2 = .996 | | | | |
| <i>T</i> = 1.0 °C | | | | |
| 10 | 0.15 | 138 | 9.1×10^{-7} | 7.6×10^{-3} |
| 11 | 0.10 | 193 | 6.5×10^{-7} | 5.4×10^{-3} |
| 12 | 0.050 | 297 | 4.2×10^{-7} | 3.5×10^{-3} |
| 13 | 0.025 | 410 | 3.1×10^{-7} | 2.5×10^{-3} |
| Statistics: ^a slope = 4.0×10^{-2} ; y-intercept = 1.5×10^{-3} ; r^2 = .999 | | | | |

^aLinear regression output from plot of k_{obs} vs. $[\text{H}^+]$.

tration of iodine formed during the reaction time period. For each reaction mixture, calculate the rate of iodine (I_2) formation ($\text{mol/L} \cdot \text{s}$) and the concentrations of H_2O_2 and I^- (mol/L). Next, calculate the logarithms of rate, $[H_2O_2]$, and $[I^-]$.

Using the values for solutions 1, 2 and 3, plot $\log(\text{rate})$ versus $\log[H_2O_2]$ and determine the slope of the line. This slope should be close to an integer, which will be the order of the reaction with respect to H_2O_2 . Plot $\log(\text{rate})$ versus $\log[I^-]$ and determine the slope, and therefore the order with respect to I^- . From the orders of the H_2O_2 and I^- , write the rate law expression for eq 1. Using this rate law, calculate the rate constant (k_{obs}) for solutions 1 through 5. The average of these k_{obs} values is the rate constant for the noncatalyzed reaction at room temperature.

Rate Law with Acid Catalysis and Activation Energies

Plot k_{obs} versus $[H^+]$ using the data collected at 25°C . The slope of this line gives the value of k_{cat} and the intercept is k_{noncat} (see eq 3). Next, construct a similar plot using the data collected at 1°C . The values of k_{noncat} and k_{cat} at the two temperatures are then used to calculate E_a for the noncatalyzed and catalyzed reactions using the Arrhenius equation.

However, as stated in the Background section, to determine the true E_a for the catalyzed reaction, one must calculate k_H while taking into account the value of K_1 and its temperature dependence. Using $k_{\text{cat}} = K_1 k_H$ and a literature value of K_1 at 25°C of 2.0×10^{-5} , one finds the value of k_H to be $8.5 \times 10^3 \text{ L/mol} \cdot \text{s}$ (considerably higher than the k_{noncat} values reported as y-intercept values in Table 3). Next, us-

ing a literature value of ΔH for the protonation of H_2O_2 ($+17.6 \text{ kJ/mol}$), one obtains a K_1 of 1.0×10^{-5} at 1°C , which yields a k_H at 1°C of $4.0 \times 10^3 \text{ L/mol} \cdot \text{s}$. Comparing these values of k_H leads to an E_a of 22 kJ/mol for the true catalyzed reaction (eq 8).

Summary

It has been shown that this variation of the iodine clock reaction is a versatile experiment. It can be used to study reaction kinetics and the influence of a catalyst. Its unique feature is that one can calculate the activation energy of the acid-catalyzed reaction independent of the noncatalyzed reaction that is occurring simultaneously. This experiment also provides the advantages of minimal chemical and equipment requirements and the ability to cater to a variety of levels of students.

Literature Cited

1. Atkins, P. W. *Physical Chemistry*, 3rd ed.; Freeman: New York, 1986; p 724.
2. Ebbing, D. D. *General Chemistry*, 5th ed.; Houghton Mifflin: Boston, 1996; p 577.
3. Zumdahl, S. S. *Chemistry*, 3rd ed.; Heath: Lexington, 1993; p 577.
4. Edwards, J. O. *Peroxide Reaction Mechanisms*; Wiley: New York, 1962; Chapter 5.
5. Liebafsky, H. A.; Mohammad, A. *J. Am. Chem. Soc.* **1933**, *55*, 3977–3986.
6. Evans, M. G.; Uri, N. *Trans. Faraday Soc.* **1949**, *45*, 224–228.
7. Edwards, J. O. *Inorganic Reaction Mechanisms*; Benjamin: New York, 1964; p 176.

Table 2. Sample Data from Noncatalyzed Reactions at 23.0°C

| Flask # | Time (s) | $[H_2O_2]$ (M) | $[I^-]$ (M) | Rate I_2 Formation (M/s) | Log Rate | Log $[H_2O_2]$ | Log $[I^-]$ | k_{obs} ($\text{M}^{-1}\text{s}^{-1}$) |
|---------|----------|----------------|-------------|----------------------------|----------|----------------|-------------|---|
| 1 | 111 | 0.0080 | 0.015 | 1.1×10^{-6} | -5.95 | -2.10 | — | 9.3×10^{-3} |
| 2 | 74 | 0.012 | 0.015 | 1.7×10^{-6} | -5.77 | -1.92 | — | 9.4×10^{-3} |
| 3 | 46 | 0.020 | 0.015 | 2.7×10^{-6} | -5.57 | -1.70 | -1.82 | 8.9×10^{-3} |
| 4 | 77 | 0.020 | 0.0090 | 1.6×10^{-6} | -5.79 | — | -2.05 | 8.9×10^{-3} |
| 5 | 113 | 0.020 | 0.0060 | 1.1×10^{-6} | -5.96 | — | -2.22 | 9.2×10^{-3} |