Kinetics Analysis of Acetone Bromination

Abstract

Beer’s law is applied to experimental chromatograph absorbance readings for distinct trials of a bromination reaction employing various concentrations of the same reactants. A rate law for the reaction is then calculated and analyzed.

Introduction

A set of trials is carried out to react specifically varied concentrations of the following standardized reactants: solution of 0.1M dissolved bromine gas, 0.1M acetone solution, and 0.1M hydrochloric acid. This gives the following reaction:

$$\text{Br}_2(\text{aq}) + \text{C}_3\text{H}_6\text{O}(\text{aq}) + \text{H}^+(\text{aq}) = \text{C}_3\text{H}_5\text{BrO}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{Br}^-(\text{aq}) \quad \text{[Equation 1.]}$$

Because molarity of the solutions is identical, equivalent volumes of the solutions give equivalent concentrations of the reactants.

Trial one, the control, involves a total reagent solution of 10 ml, with ten percent volume each of the bromine, acetone, and hydrochloride solutions. Each of the following three trials also involves 10 ml total solution, but reacts double the volume of one experimental reactant while maintaining the others at ten percent volume each, as imposed by the control. Each solution is mixed by thoroughly shaking; a sample is placed in a beaker and this in turn is placed in a chromatograph that in effect measures the amount of Bromine gas remaining in solution as the reaction progresses over time (see method), outputting a graph of absorbance versus time for each trial run (see results).

By analyzing the graphs output for each trial run, slopes can be determined and standardized to give reaction rate (Re, the numerator in equation 2) for each trial. Rc is the rate for the control reaction involving equal concentrations, and hence equal numbers of each participant reactant in equation 1. The orders x, y, and z of each reactant concentration in all the equations as they contribute to reaction rate is determined by setting up a proportion between the control trial rate law versus the experimental trial rate law for each experimental trial:

$$\text{Re} = k[n\text{Br}_2]^x[n\text{Acetone}]^y[n\text{HCl}]^z$$

$$\text{Re} = k[\text{Br}_2]^x[\text{Acetone}]^y[\text{HCl}]^z \quad \text{[Equation 2.]}$$

By varying only one reactant concentration in each Re, the constants and reactants maintained at control level cancel, giving a logarithmic equality that produces the order of the one varied reactant concentration. Finally, a rate law constant may be calculated knowing the order of reactant concentrations in the established rate law. The rate law constant should be roughly equal for all trials and may be averaged to reflect the total experimental observations. This constant is only accurate assuming constant conditions, or the average conditions (especially room temperature).
Method

A chromatograph is standardized for zero absorbance of 400nm wavelength light through deionized water because bromine gas effectively absorbs 400nm wavelengths. Three test tubes are used to hold the standard reactant solutions, while a fourth holds deionized water used to standardize the solution volume and thus percent concentration of reactants in the observed solutions. Three graduated glass pipettes are used to avoid cross-contamination while measuring the standard 0.10M reactant solutions of bromine, acetone and hydrochloride, while a fourth measures the deionized water mixed into the observed solutions. In the control, 1.0 mL each reactant is used, and in the three experimental trials, 2.0 mL of one reactant to 1.0 mL each of the remaining two reactants is used. The water standardizes volume of the total observed solution to 10. mL, giving a control concentration of each reactant as 0.010M). A graduated beaker with clean stopper is used to verify total solution volume and to mix reactants.

A fraction of the mixed solution is placed in a beaker compatible with the chromatograph, and an attached computer is activated to begin interpreting digitally transmitted results, plotting absorbance changes over three hundred seconds time. The reaction may or may not complete, but the graph gives the slope necessary to find the rate of reaction necessary to draw conclusions about the kinetics of the experimental reaction.

Results

Graph 1: Control Trial Using Equal Concentrations of All Reactants

Trial one unfortunately used an overfilled chromatograph beaker that was wet with isolated reactants outside the chromatograph beaker. Thus, as these passed between absorbance detectors for some of the trial time, increasing absorbance was recorded. Later, evaporation and isolated reaction in this adhesive solution likely caused a faster drop-off of absorbance. To eliminate this error, only the interval from 170 to 220 seconds was used to calculate rate and to give the red slope like shown above.
Graph 2: Experimental Doubling of Acetone (Interval 0-260s)

Graph 3: Experimental Doubling of Hydrochloride (Interval 10-300s)
**Graph 4:** Experimental Doubling of Dissolved Bromine Gas (*Interval 10-300s*)

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**Results (Continued)**

Graph two slope was determined for the interval 260-0s because the reaction completed between 260s and 270s as shown on the graph.

Graphs three and four discounted the first ten second interval because recording began while the chromatograph recording the reaction was still open, giving a lower absorbance reading not related to the reaction rate.

Beer’s Law states that absorbance is proportional to concentration, so the absorbance decrease is the concentration decrease of bromine in the reaction. By equation 1, the concentration decrease of acetone and protons in solution is identical to this decrease. Examining each analyzed interval on the graphs, it is seen that the points plotted within these intervals are roughly linear. Thus, the inverse of concentration plotted over time is linear, and it becomes apparent that the overall reaction order is two.

Exact slopes are given in the calculation of delta y values for the time (x) intervals used in trials 1-4:

[Calculation set 1.]

\[
\begin{align*}
\Delta y_1 &= 0.810 - 0.894 = -0.0840; \\
\Delta y_2 &= 0.0200 - 1.00 = -0.980; \\
\Delta y_3 &= 0.0587 - 1.104 = -1.045; \\
\Delta y_4 &= 1.633 - 2.12 = -0.487
\end{align*}
\]

Normalizing the above slopes to give rate per minute of bromine decrease gives the following experimental reaction rates:
By writing the rate law equation with variable orders for the individual reactants, a proportion can be setup between the control law and experimental law concentration, for each reactant (see introduction, equation 2). The remaining equality gives the order of the reactant in that equality. Note that molarity in solution is the concentration with respect to the entire solution of 10 mL.

Bromine order: \( R_\text{Br}/R_\text{Br}_\text{4} (-0.101/-0.101 = 1) \); \([\text{Br}_2]^x = [2\text{Br}_2]^x\), \(([0.01]/[0.02])^x = 1\)
Therefore, \(x=0\).

Acetone order: \( R_\text{A}/R_\text{A}_\text{1} (-0.226/-0.101 = 2.24)\); \(([0.01]/[0.02])^y = 2.24\)
\((y=\log_{0.5} 2.2436 = 1.12)\) Rounded to an integer order, \(y=1\).

\(\text{H}^+\) order: \( R_\text{H}^+/R_\text{H}^+ (0.2162/-0.101 = 2.14)\); \(([0.01]/[0.02])^z = 2.14\)
\((z=\log_{0.5} 2.14 = 1.10)\) Rounded to an integer order, \(z=1\).

Thus, the rate law for the reaction being analyzed is determined to be

\(R = k[C_3H_6O][\text{H}^+]\). Solving for the rate law constant of each trial gives:

\(k_\text{1} = -0.101/((1)(0.01)(0.01)) = -1010\)
\(k_\text{2} = -0.226/((1)(0.02)(0.01)) = -1130\)
\(k_\text{3} = -0.2162/((1)(0.01)(0.02)) = -1081\)

\(k_{\text{average}} = (2(-1010) - 1130 - 1080) / 4 = 1060\)

Conclusions

It is interesting that both the orders for acetone and proton concentration are calculated to be above one and then rounded down. It corresponds that their experimental determined rates of reaction are slightly more than double (<13%) the control reaction rate. The difference for protons may be partly explained by the auto-ionization of water, but this is on a smaller order and deionizing agents in the deionized water may still have an effect in the solution. If the balanced equation 1 is correct, it would be possible that the reaction equilibrium would tend to slow the rate as proton concentration increases, but this is not the case. The difference for acetone may have to do with its volatility. Because the partial pressure would be higher for the experimentally doubled concentration (in trial 2), not as much acetone may evaporate before or during this reaction, giving more than double the reaction rate of the control. In order to verify the experimentally determined order of the reaction in future experiments of this type, it might be advisable to repeat the set of three experimental runs using triple and quadruple concentrations. Nonetheless, from the data collected, it becomes apparent that hydrogen must form an intermediate product with bromine so that as long as some bromine is present, this intermediate product may successfully collide with either acetone or an intermediate acetone product to give the final product of brominated acetone.