Reaction Kinetics. The Bromination of Acetone

REFERENCES
Physical Chemistry, Atkins, 1994 Chapter 25
Physical Chemistry, Levine, 4th edition 1995 Chapter 17

PURPOSE:
The purpose of this experiment is to determine the rate law and the rate constant for the bromination of acetone. From rate data collected at two or more temperatures, the activation energy is determined.

DISCUSSION:
The bromination of acetone in acid solution proceeds according to

\[ \text{CH}_3\text{C(O)CH}_3 + \text{Br}_2 \xrightarrow{\text{H}^+} \text{CH}_3\text{C(O)CH}_2\text{Br} + \text{Br}^- + \text{H}^+ \] \[1.\]

The reaction is catalyzed by hydrogen ion. The rate law is assumed to be of the form

\[ \text{rate} = \frac{-d[\text{acetone}]}{dt} = \frac{-d[\text{Br}_2]}{dt} = k[\text{acetone}]^p[\text{Br}_2]^q[\text{H}^+]^r \] \[2.\]

where \(k\) is the rate constant and \([A]\) represents concentration of \(A\) in moles liter\(^{-1}\). The exponents \(p\), \(q\), and \(r\) indicate the order of the reaction with respect to acetone, bromine, and hydrogen ion, respectively.

The bromination of acetone is a particularly convenient and interesting reaction to study kinetically. The progress of reaction is readily followed by directly observing the decrease in bromine concentration spectrophotometrically at a wavelength where none of the other reagents has significant absorption. Further, the reaction provides a remarkable demonstration of the general rule that it is not possible to predict the rate law from just the knowledge of the stoichiometric equation. As will be confirmed in this experiment, the reaction is zero order in bromine, i.e., \(q\) in equation [2] is zero. This result provides a straightforward application of the method of initial rates wherein the acetone and acid are present in large excess while the bromine is used in small concentrations to limit the extent of reaction. The small amount of bromine is completely consumed while the other reactants remain at an essentially constant concentration. Since the reaction velocity is independent of the bromine concentration the rate is constant until all of the bromine is consumed. Under these conditions

\[ \text{rate} = \frac{-d[\text{Br}_2]}{dt} = k[\text{acetone}]^p[\text{H}^+]^r \] \[3.\]

and therefore a plot of \([\text{Br}_2]\) against time is a straight line whose slope is the reaction rate.

For the determination of the exponent \(p\) it is necessary that the reaction be followed in two runs in which the initial concentrations of acetone are different while the initial concentrations of hydrogen ion are not changed from one run to the next. Using

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1 This experiment has been adapted from Crockford et al., *Laboratory Manual of Physical Chemistry*, 1982.
subscripts I and II to denote the two experiments, we have \([\text{acetone}]_I = u \times [\text{acetone}]_{\text{II}}\) and \([\text{H}^+]_I = [\text{H}^+]_{\text{II}}\). Then from equation [3], we have

\[
\frac{\text{rate}_I}{\text{rate}_I} = \frac{k[\text{acetone}]_I [\text{H}^+]_I}{k[\text{acetone}]_I [\text{H}^+]_I} = \frac{u^p[\text{acetone}]_I}{[\text{acetone}]_{\text{II}}} = u^p
\]

which yields

\[
\ln(\frac{\text{rate}_I}{\text{rate}_I}) = p \ln(u)
\]

or

\[
p = \frac{\ln(\frac{\text{rate}_I}{\text{rate}_I})}{\ln(u)}
\]

The exponent \(r\) is determined from two runs, say I and III, in which \([\text{acetone}]_I = [\text{acetone}]_\text{III}\) and \([\text{H}^+]_I = w \times [\text{H}^+]_I\). These conditions lead to

\[
r = \frac{\ln(\frac{\text{rate}_I}{\text{rate}_I})}{\ln(w)}
\]

the rate constant is then determined according to equation [2] from the exponents, reaction rate, and the concentration data for which the rate applies. The activation energy \(E\) may be estimated from the Arrhenius relationship:

\[
k = A \exp(-E_a/RT)
\]

if the rate constant is known at several temperatures. The empirical rate law is assumed to hold at the other temperatures so that one needs only to measure the rate for a set of known concentrations at each temperature of interest. The bromine concentrations are determined from measurements of the absorption of blue light by the solutions. The absorbance is given by

\[
A = \varepsilon bc
\]

where \(\varepsilon\) is the molar absorptivity, \(b\) is the sample path length in centimeters, and \(c\) is concentration in moles per liter. For \(\text{Br}_2\) dissolved in distilled water \(\varepsilon\) equals \(\sim 80\ M^{-1}\text{cm}^{-1}\) at 400 nm. The absorbance should be in the range of 0.7 to 0.2 for greatest accuracy. Since cuvettes commonly have a sample path length of 1 cm, the desired concentration range for bromine in the reaction mixture is from 0.0044 \(M\) to 0.0012 \(M\). For cuvettes that have been selected for close matching of path length, the constant \(\varepsilon\) and \(b\) of equation [9] may be taken together as a constant \(B\) to give

\[
A = Bc
\]

It is recommended that the constant \(B\) be determined experimentally.

APPARATUS AND CHEMICALS:
Spectrophotometer, pipettes, volumetric flasks, glass stoppered bottles, glass stoppered 125-ml Erlenmeyer flasks, stopwatch, constant temperature bath, potassium bromate & potassium bromide or bromine stock solution, 4\(M\) acetone, 1\(M\) hydrochloric acid.

EXPERIMENTAL PROCEDURE:
All absorbance measurements are to be made at 400 nm. The instructor will provide instructions on the use of the spectrophotometer. Handle solutions containing bromine with care, and do not let it contact your skin, it burns. If burned, see the
instructor immediately. Wear gloves. Also be cautious with the vapor, keep solutions stoppered.

**Determination of the B constant:** The constant B of equation [10] is determined by measuring the absorbance of at least three solutions of known bromine concentration. At room temperature, prepare one solution by pipetting 10.0 ml of stock 0.02 $M$ Br$_2$ into a clean 125-ml Erlenmeyer flask. Add 10.0 ml of 1 $M$ HCl and 30.0 ml of distilled water. Mix the solution thoroughly and measure the absorbance. Repeat this procedure using first 6.0 ml and then 3.0 ml of 0.02 $M$ Br$_2$ diluted in each case with 10.0 ml of 1 $M$ HCl and sufficient distilled water to give a total volume of 50.0 ml of solution. Record the three values of absorbance and concentration.

**Reaction mixtures:** Keep all reagent solutions thermostatted in a water bath at the temperature you are working at. Start at 25°C and measure the reaction rate at least twice for each of the four different solutions shown below in Table 1. You will need a fresh mixture each time. Why? Be sure the temperature of the sample cell in the spectrometer is the same as the thermostat.

The appropriate quantities of acetone and hydrochloric acid are first mixed together in a 125 ml Erlenmeyer flask. The reaction starts as soon as the bromine water and acetone mix in the flask. Stir the reaction mixture thoroughly and quickly. Rinse a clean cuvette quickly with the reaction mixture, fill it and place it in the spectrophotometer. Record the absorbance as a function of the time until the absorbance falls below about 0.1. Record the temperature of the solutions. Satisfactory reaction solutions are prepared as shown in Table 1. For each solution add distilled water to make a total volume of 25 ml.

**TABLE 1**

<table>
<thead>
<tr>
<th>Solution Number</th>
<th>0.02 $M$ Br$_2$</th>
<th>4.0 $M$ Acetone</th>
<th>1.0 $M$ HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 ml</td>
<td>5ml</td>
<td>5ml</td>
</tr>
<tr>
<td>2</td>
<td>5 ml</td>
<td>2ml</td>
<td>5ml</td>
</tr>
<tr>
<td>3</td>
<td>5 ml</td>
<td>5ml</td>
<td>2ml</td>
</tr>
<tr>
<td>4</td>
<td>10 ml</td>
<td>5ml</td>
<td>5ml</td>
</tr>
</tbody>
</table>

Early in the laboratory period place some of each of the stock solutions and distilled water in the constant temperature baths at the desired higher temperatures (35°C and 45°C are suitable) and allow sufficient time for them to reach thermal equilibrium. The proper quantities of acetone, hydrochloric acid, and distilled water may be mixed before placing them in the constant temperature bath. Use reaction mixture number 2 at the higher temperature. Mix the solutions and record absorbance and time as was done for the solutions at room temperature. Record the temperature of the water baths.

**DATA ANALYSIS:**
From the absorbance -measurements on the three solutions of bromine water determine an average value of B in equation [10]. Use this result to compute the concentration of bromine for each absorbance reading in the kinetic runs. For each run prepare a plot of [Br$_2$] against time and determine the rate

\[
rate = \Delta [Br_2]/\Delta t
\]

[11.]
Equations [6] and [7] are used to compute the order of reaction with respect to acetone and with respect to hydrogen ion. An analogous equation is used along with the data on solutions number 1 and number 4 to calculate the order with respect to bromine. Use equation [3] and the experimental results obtained to calculate the rate constant $k$ for each of the kinetic runs. Determine an average value of $k$ for each temperature used in the experiment. Make an Arrhenius plot (that is, $\ln k$ vs $1/T$). The slope, which equals $-E_a/R$ yields the activation energy, and the intercept yields the preexponential term, $A$. (Be careful with units!)

COMMENTS TO THE INSTRUCTOR:
The investigation of the kinetics of this reaction is reported by A. Lapworth in *J. Chem. Soc.*, 85, 30 (1904).

It is recommended that the bromine stock solution be prepared before the laboratory period. The solution is prepared from the reaction of potassium bromate and potassium bromide. Weigh on the analytical balance enough pure, dried potassium bromate ($\text{KBrO}_3$, 167.0 g mol$^{-1}$) to provide one-third as many moles of bromate as the moles of bromine ($\text{Br}_2$) which are desired in the final stock solution. Transfer this to the proper volumetric flask.

To this add a weighed amount of potassium bromide ($\text{KBr}$, 119.0 g mol$^{-1}$) representing five times as many moles of bromide as the moles of bromate already weighed. Transfer this to the same volumetric flask. Fill about half-full with distilled water and dissolve the salts with swirling. Add, slowly with gentle swirling, 0.7 ml of 3 $M$ $\text{H}_2\text{SO}_4$ for each 0.100 gram of bromate used. Fill to the mark with distilled water, stopper and mix thoroughly. Store the solution in a glass stoppered bottle. The $\text{Br}_2$ is not fully released for an hour or more.

Students should be specifically cautioned concerning the hazards of bromine vapors and solutions of bromine. If the solution comes in contact with the skin, the affected portion of skin should be bathed with ethanol (65%) and then with glycerin.