

The Kinetics of the Acid-Catalyzed Bromination of Acetone

Introduction

The initial reaction between bromine and acetone is written:



In neutral solution the reaction is slow, but in the presence of either acid or base an appreciable increase in the reaction rate occurs. The reaction rate is exactly the same for bromine, chlorine and iodine and is independent of the concentration of halogen present.

In this experiment you determine (or confirm) the dependence of reaction rate on the concentrations of bromine, acetone, and hydrochloric acid. The simplest way of doing this is to adopt the isolation technique, in which you carry out a series of rate observations keeping two of the three concentrations constant in each set of measurements, while varying the other. In order to simplify the treatment of the results you will measure and use only the initial rate in each run.

In the reaction it is convenient to follow the concentration of bromine spectrophotometrically. To do so we will make use of Beer's law:

$$A = \log(I_0/I) = \epsilon c l \quad (\text{II.2})$$

where A is the absorbance, I_0 is the light intensity impinging on the sample, I is the light transmitted through the sample, c is the concentration of the absorbing species, l is the path length of the absorbing solution, and ϵ is called the extinction coefficient or molar absorption coefficient.

Procedure

1. Measurement of the molar extinction coefficient of bromine in aqueous solution at 450 nm.
 - a. Run 10.00 ml of the saturated bromine solution from the stock burette (be sure that you flush the delivery tip each time to avoid errors due to the volatility of bromine) into a 250-ml Erlenmeyer flask containing approximately 50 ml of 10% potassium iodide solution. Titrate the mixture with standard (0.100 N) sodium thiosulfate solution. Run in the thiosulfate solution until a faint yellow color remains; at this point add approximately 5 ml of starch indicator solution (0.2 g starch per 100 ml or 1 packing peanut in 100 ml water) and carefully continue adding the thiosulfate until the dark blue color disappears, giving a colorless solution.
 - b. Run 10.00 ml of the saturated bromine solution into about 40 ml of water contained in a 100-ml volumetric flask. Make up to the mark with water, mix well and measure the absorbance of this solution at 450 nm, using water as the blank.

2. Measurement of the rate of bromination of acetone.

Make up the necessary solutions - one at a time, just prior to measurement - in clean, 100-ml volumetric flasks.

First add about 40 ml of water to the 100-ml volumetric flask and then run in the requisite volumes of saturated bromine solution, 1.00 M hydrochloric acid and acetone from the stock burets. Make up to the mark with water and quickly attain homogeneity by efficient mixing. Transfer a sample to the absorbance cell for the rate measurement. For a blank, it will be satisfactory to use a 100.0-ml mixture of 5.00 ml acetone, 10.0 ml of 1.00 M HCl, and the remainder water, for all the rate studies.

Open the HP UV/VIS spectrophotometer program and load the method "302BR.M". This method initializes the spectrometer to perform a kinetics measurement over 3 minutes and to determine the initial rate using a linear fit. Measure a blank first, click on "time based measurement", mix your solution, insert the cuvette and hit "start".

For maximum precision the reaction should be followed with the absorbance cells maintained at constant temperature. Here, however, the various solutions will have been made up sometime previously so that they will all be at the same (room) temperature. After each rate run, measure and record the temperature in the absorbance cell as well as the room temperature. The mean of these two temperatures may be taken as the reaction temperature. Using care and common sense, the lack of temperature control will not be a serious difficulty.

The actual amounts of bromine solution, acetone and hydrochloric acid to be used are left up to the individual experimenter. Arrange these so as to determine the three dependencies with as few runs as possible. If necessary, repeat each run more than once, to obtain a reasonably reproducible control rate. In general, all runs can be completed in about ten minutes. Plot results after each run.

As an assist in making up a schedule of the different solutions, note that the following relative amounts proved satisfactory when the concentration of the "saturated" bromine solution was ≈ 0.09 M. You may need to adjust the volumes if your saturated bromine solution is a different concentration. Absorbances between 0.1 and 0.9 are best.

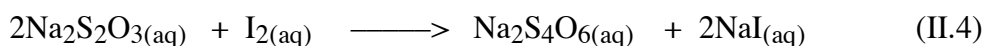
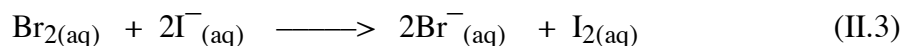
Table I. Reasonable volumes for use with 0.09 M bromine solution

	<u>Saturated Br₂ solution</u> (ml)	<u>Acetone</u> (ml)	<u>1.00 M HCl</u> (ml)
(1)	3	5	10
(2)	6	5	10
(3)	9	5	10
(4)	9	5	5
(5)	9	5	20
(6)	9	10	20
(7)	9	20	20

Treatment of experimental data

1. Determine the concentration of the saturated bromine solution from your thiosulfate titration value.

The redox reactions are:



Make sure that you understand the end point in your titration. Starch and iodine form a dark blue complex.

2. Calculate the absorption coefficient of bromine in aqueous solution
3.
 - a. Tabulate the initial rates $(dA/dt)_0$ in the attached worksheet.
 - b. Study the various initial rates $(dA/dt)_0$ and thus confirm the independence of the reaction rate on the concentration of bromine.
 - c. Show that your values of $(dA/dt)_0$ are in conformity with first order kinetics for both acetone and hydrochloric acid.
4. The rate equation can therefore be written:

$$\text{Rate} = -\frac{d[\text{acetone}]}{dt} = k[\text{acetone}][\text{HCl}] \quad (\text{II.5})$$

- a. For each value of $(dA/dt)_0$, calculate the rate in moles of bromine reacting per minute per liter.
- b. For each value of $(dA/dt)_0$, calculate the rate constant k using the expression

$$k = \frac{(dA/dt)_0}{[\text{acetone}]_0[\text{HCl}]_0} \quad (\text{II.6})$$

Write-up

1. Summarize your results in the data table (page II-4) that includes the volumes of each of the reagents used, the initial rate, the moles of Br_2 reacting per minute, and the rate constant.
2. Include a general discussion of the kinetics and mechanism of the halogenation of acetone in acidic and basic solution.
3. Is your proposed mechanism consistent with the observed rate law?

Safety Note

Bromine is corrosive and highly toxic. Bromine solutions should be confined to a fume hood as much as possible. Save your reaction solutions until all reactions have been completed. When you are completely finished, dispose of the reaction solutions in the waste container for this experiment.

Reference

R.T. Morrison and R.N. Boyd, *Organic Chemistry* (Allyn and Bacon, Boston, 1973) pp 706-8.

Feb-91 JT; Jan-92 epl; Apr-03; DB

Your Name _____ Date _____

Your Partner(s) _____

Concentration of saturated bromine solution _____ M

Molar absorptivity of bromine solution at 450 nm = ϵ_{450} = _____ $M^{-1} \text{ cm}^{-1}$

In 100.0 ml of solution:

Saturated Br ₂ solution (ml)	Acetone (ml)	1.00M HCl (ml)	Initial Rate $-(dA/dt)_0$	Mole/L Br ₂ reacting per min per liter	Rate Constant ($M^{-1} \text{ min}^{-1}$)
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____

Average rate constant = _____

The literature value for the rate constant at 25°C is $1.7 \times 10^{-3} M^{-1} \text{ min}^{-1}$

Deviation from literature value = _____

Be sure to note the uncertainties in each of the columns of your data table. Briefly comment on anything noteworthy in your data.

From the 344 Kinetics Method, set wavelength at 450 nm, and go to the Time button under the “lamp”, and open a data file to store data. Then run the time measurements