

Method of initial rates in the bromination of acetone

Introduction [1]

Method of initial rates

Several methods exist for determining the rate law for a chemical reaction. One of the most powerful methods is the method of initial rates [2]. Consider the following chemical reaction



where A, B, and C are reactants, D, E, and F are products, and a, b, ..., f are the stoichiometric coefficients for the chemical reaction. The rate of the reaction, R, is defined as

$$R = - (1/a) d[A]/dt = - (1/b) d[B]/dt = \dots = (1/f) d[F]/dt \quad (2)$$

Note that the rate of the reaction can be given either in terms of the rate of disappearance of a reactant or the rate of appearance of a product. Note also that the rates of appearance or disappearance are weighted by the stoichiometric coefficients of the reaction.

The rate law for the chemical reaction is an expression that gives the rate of the reaction as a function of the concentrations of reactants and products, and of temperature.

$$R = f(A, B, \dots, F, T) \quad (3)$$

In fact, the rate law may also depend on the concentrations of molecules that appear neither as products nor as reactants (as in the case of a catalyst), on the solvent in which the reaction occurs, and on other parameters as well.

For a large number of chemical reactions, it has been found that the general (and not very useful) relationship given in equation (3) takes the following simple form

$$R = k [A]^p [B]^q [C]^r \quad (4)$$

where k is the rate constant for the reaction, which is a function only of temperature, and [A], [B], ... are concentrations of substances on which the rate of reaction is dependent. The coefficients of these concentrations, p, q, ... are called the order of the reaction with respect to [A], [B], ..., while the sum of the coefficients, p + q + ... is called the overall reaction order. It should be emphasized that equation (4) is based on observation, and that there are many chemical reactions that do not follow such a simple rate law. Also, as noted above, there is no reason why equation (4) might not include a dependence on the concentration of a product molecule or of a catalyst.

Consider the initial rate of reaction for a system that obeys the rate law given in equation (4). If the initial concentrations of A, B, and C are $[A]_i$, $[B]_i$, and $[C]_i$, then the initial rate of the chemical reaction, R_i , is

$$R_i = k [A]_i^p [B]_i^q [C]_i^r \quad (5)$$

As the reaction proceeds and reactants are converted into products, the concentrations of A, B, and C will decrease. However, if the rate of reaction is measured before the reaction has had a chance to proceed very far, the rate of reaction will be given by equation (5). The usefulness of equation (5) lies in the fact that it is often possible to select experimental conditions such that the initial concentrations of reactants are known, which allows the determination of the rate law from experimental measurements, as discussed below.

Consider the initial rate of reaction for two sets of starting conditions, with subscripts 1 and 2, and at the same temperature.

$$R_1 = k [A]_1^p [B]_1^q [C]_1^r \quad (6)$$

$$R_2 = k [A]_2^p [B]_2^q [C]_2^r \quad (7)$$

If we divide equation (7) by equation (6), we get

$$R_2/R_1 = ([A]_2/[A]_1)^p ([B]_2/[B]_1)^q ([C]_2/[C]_1)^r \quad (8)$$

Now assume in selecting the initial concentrations of reactant molecules we choose $[B]_1 = [B]_2$ and $[C]_1 = [C]_2$, that is, only the initial concentration of A is allowed to change. All terms not involving the concentration of A will drop out of equation (8), leaving

$$R_2/R_1 = ([A]_2/[A]_1)^p \quad (9)$$

or, taking the natural logarithm of both sides of the equation and solving for p

$$p = \ln(R_2/R_1)/\ln([A]_2/[A]_1) \quad (10)$$

By comparing the initial rate of reaction under conditions where the initial concentration of A has been varied while the initial concentration of other reactants has been held constant, we have been able to determine the order of the reaction with respect to A. By a similar procedure, we may also determine the reaction order with respect to B and C. Once the reaction orders are known, the value for the rate constant can be found by solving equation (5) for k.

When there is a large amount of experimental data available, a better method for determining the reaction orders can be found. The starting point is once again equation (5). If we take the natural logarithm of both sides of equation (5), we get

$$\ln(R_i) = \ln k + p \ln[A]_i + q \ln[B]_i + r \ln[C]_i \quad (11)$$

Taking the partial derivative of R_i with respect to $[A]_i$ gives

$$p = \partial \ln(R_i) / \partial \ln([A]_i) \quad (12)$$

What equation (12) tells us is that if we plot $\ln(R_i)$ vs $\ln([A]_i)$ for a set of experimental conditions where all other initial concentrations have been held constant, the slope of the resulting best fitting line to the experimental data will be equal to p, the order of the reaction with respect to A. Again, a similar procedure may be used to find the order of the reaction with respect to B, C, and so forth.

Bromination of acetone reaction

The chemical reaction for the bromination of acetone in aqueous solution has the following stoichiometry



The rate law for this reaction may be written as

$$R = k [\text{H}^+]^p [\text{CH}_3\text{COCH}_3]^q [\text{Br}_2]^r \quad (14)$$

where we have taken into account in the rate law the fact that reactions of this type are often acid catalyzed. This particular reaction is known to be zeroth order in Br_2 ($r = 0$), and so the rate law becomes

$$R = k [\text{H}^+]^p [\text{CH}_3\text{COCH}_3]^q \quad (15)$$

In addition, since we are working in this experiment under conditions where the initial concentrations of hydrogen ion and acetone are much larger than the concentration of bromine present, both $[\text{H}^+]$ and $[\text{CH}_3\text{COCH}_3]$ remain approximately constant throughout the course of the bromination reaction. That means that the rate of the reaction for

a particular set of initial conditions is also approximately constant, simplifying the determination of the rate of reaction.

The purpose of the present experiment is to determine the order of the bromination reaction with respect to hydrogen ion and acetone, and to then find the value for the rate constant for the reaction.

Experimental

Stock solutions of bromine, hydrogen ion, and acetone are prepared as follows:

Bromine - The 0.02 M Br₂ stock solution is prepared by the chemical reaction of bromate ion (BrO₃⁻) with bromide ion (Br⁻). To make 250 mL of bromine stock solution, weigh out 0.278 g of KBrO₃ and 0.992 g of KBr. Add these compounds together in a 250 mL volumetric flask. Half fill the volumetric flask with water and swirl to dissolve the salts. Add 2 mL of 3 M H₂SO₄ to the volumetric flask, and then fill to the mark with distilled water. The chemical reaction that produces Br₂ takes approximately two hours to go to completion.

Hydrogen ion - To make 250 mL of 1.0 M HCl stock solution carefully dilute 20.0 mL of concentrated HCl to a final volume of 250 mL in a volumetric flask.

Acetone - To make 250 mL of 4.0 M acetone stock solution dilute 73.4 mL of reagent grade acetone to a final volume of 250 mL in a volumetric flask.

Absorption measurements will be carried out on either a double beam UV-visible spectrophotometer or a single beam Spec 20 spectrophotometer. The instrument should be allowed to warm up for at least 15 minutes prior to the first experimental measurements. If the cuvette holder of the spectrophotometer is connected to a temperature bath, set the bath temperature to 20. °C. The spectrophotometer should be zeroed at 400 nm by the method appropriate for the instrument used, with deionized water used as a reference or blank. During the kinetic runs the sample cuvette will be filled with a sample of the solution in which the bromination reaction is taking place, while the reference cuvette (if used) will remain in place and filled with deionized water.

The reaction rate will be found for four conditions where all initial concentrations except that of hydrogen ion are held constant, and four conditions where all initial concentrations except that of acetone are held constant (solution 1 can be used in both of the determinations of the reaction order). A table listing the volumes of each stock solution to be used in each trial is given on the next page. All solutions should be made up to a final volume of 50 mL by addition of distilled water. The solutions are prepared by mixing the appropriate amounts of each stock solution as indicated above, in the order HCl stock solution, acetone stock solution, deionized water, and bromine stock solution. **DO NOT ADD THE BROMINE STOCK SOLUTION UNTIL JUST PRIOR TO THE START OF EACH OF YOUR MEASUREMENTS.**

After adding bromine to the solution, mix rapidly, then fill a cuvette with solution. Measure the initial absorbance of the solution (at 400 nm) on a spectrophotometer. This initial absorbance is expected to be $A \cong 0.7$. Continue to make absorption measurements at one minute intervals for a period of 10 minutes, or until the initial absorbance has decreased to below 0.05.

For each experimental condition plot absorbance against time to determine dA/dt , the rate of change of absorbance as a function of time. Since Beer's law states

$$A = \epsilon c \ell \quad (16)$$

(where A = absorbance, ϵ = extinction coefficient, c = concentration of absorbing species, and ℓ = path length of the sample cell), we may show that the rate of change of the concentration of Br₂ with time, $d[\text{Br}_2]/dt = dc/dt$, is given by the expression

$$dc/dt = (1/\epsilon\ell) dA/dt \quad (17)$$

The extinction coefficient (also sometimes called the absorption coefficient) for Br₂ at 400 nm is $\epsilon = 160$. L/mole•cm. None of the other chemical species absorb light at this wavelength. The pathlength for the cuvette or sample tube is $\ell = 1.0$ cm.

Since ϵ and ℓ are known, equation (17) can be used to find the rate of change in bromine concentration with time. Since bromine is a reactant, the rate of the reaction for each trial is

$$\text{Rate} = -d[\text{Br}_2]/dt \quad (18)$$

By analyzing the experimental data as suggested by equation (12), determine the order of the reaction with respect to hydrogen ion and acetone. After the reaction orders have been found, determine the value of the rate constant for the reaction. When determining the value of the rate constant for the bromination reaction, you should first round off the experimental reaction orders to the nearest integer values. In doing so, one is making the assumption that the reaction mechanism is fairly simple and does not lead to fractional reaction orders or otherwise complicated rate laws, and thus that nonintegral exponents are the result of experimental error. This is the case for the bromination of acetone and is the most common case; more complicated rate laws would require more extensive work to determine.

Note that, if the absorbance stops changing, reaction is essentially complete. Should you include points in your fit after reaction is complete? Note also that the above procedure for determining the rate law for the bromination of acetone reaction is valid only because the rate law is zeroth order with respect to Br₂, and because we have chosen to work under conditions where $[\text{H}^+], [\text{CH}_3\text{COCH}_3] \gg [\text{Br}_2]$. As a consequence of this, a plot of absorbance vs time (which is equivalent to a plot of bromine concentration against time) gives a straight line whose slope is related to the rate of the reaction. You should think about how changing either of the above two conditions would affect your observed experimental results.

TABLE 1. Experimental conditions for kinetic runs.

Solution	1.0 M HCl	4.0 M acetone	dH ₂ O	0.020 M Br ₂
1	10 mL	10 mL	20 mL	10 mL
2	15 mL	10 mL	15 mL	10 mL
3	20 mL	10 mL	10 mL	10 mL
4	25 mL	10 mL	5 mL	10 mL
5	10 mL	15 mL	15 mL	10 mL
6	10 mL	20 mL	10 mL	10 mL
7	10 mL	25 mL	5 mL	10 mL

Lab Report

Your lab report should include the following:

- 1) A table containing your raw data (absorbance vs time for each trial).
- 2) A plot of absorbance vs time for each trial, and an explanation of how the observed rate of reaction was obtained from these plots.
- 3) The details (including any data plots) for your determination of the order of the reaction with respect to H⁺ ion and acetone.

4) The average value and 95% confidence limits for k, the rate constant for the reaction, including correct units, along with an explanation of how these results were obtained.

5) A comparison of your experimental results (reaction orders and rate constant) with literature values [3].

References

1. A general discussion of chemical kinetics is given in Chapters 20 of P. W. Atkins, J. de Paula Physical Chemistry, Tenth Edition, (Freeman, New York, 2014).

2. Atkins and de Paula, p. 825.

3. The following reference can be found online through the FIU library website.

Rice, F. O. and C. F. Fryling, J. Amer. Chem. Soc. *47* (1925) 379-384. On p. 380, under “previous work” the orders of the reaction with respect to H⁺ and acetone are given. A value for k, at T = 25 °C, is given in Table 1. The units are not given (and no error limits are stated), but the value is 17.12×10^{-4} L/mol•min.