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

$$a\,A + b\,B + c\,C \rightarrow d\,D + e\,E + f\,F \tag{1}$$

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

$$R = -\,(1/a)\,d[A]/dt = -\,(1/b)\,d[B]/dt = \ldots = (1/f)\,d[F]/dt \tag{2}$$

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.

$$R = f(A, B \ldots, F, T) \tag{3}$$

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

$$R = k\,[A]^p\,[B]^q\,[C]^r \tag{4}$$

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

$$R_i = k\,[A]_i^p\,[B]_i^r\,[C]_i^r \tag{5}$$

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.

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

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

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

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

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

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

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

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

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

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

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

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

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

$$CH_3COCH_3 + Br_2 \rightarrow CH_3COCH_2Br + H^+ + Br^- \qquad (13)$$

The rate law for this reaction may be written as

$$R = k\,[H^+]^p\,[CH_3COCH_3]^q\,[Br_2]^r \qquad (14)$$

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

$$R = k\,[H^+]^p\,[CH_3COCH_3]^q \qquad (15)$$

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 $[H^+]$ and $[CH_3COCH_3]$ 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

Absorption measurements will be carried out on either a double beam UV-visible spectrophometer 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. Data should be taken as absorbance vs time at a fixed wavelength of 400 nm, at one minute intervals, for 10 minutes or until the initial absorbance has decreased to less than 0.05 .

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

Bromine - The bromine stock solution is prepared by the chemical reaction of bromate ion (BrO_3^-) with bromide ion (Br^-). To make 250 mL of 0.02 M Br_2 stock solution, weigh out 0.278 g of $KBrO_3$ 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 H_2SO_4 to the volumetric flask, and then fill to the mark with distilled water. The chemical reaction that produces Br_2 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.

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 YOUR MEASUREMENT**. After preparing the solution, mix rapidly, then fill a cuvette with solution. Measure the absorbance of the solution (at 400 nm) versus time on a spectrophotometer. The extinction coefficient (also sometimes called the absorption coefficient) for Br_2 at 400 nm is $\varepsilon = 160.$ L/mole-cm. None of the other chemical species absorb light at this wavelength. Continue the absorbance measurements until the absorbance falls to about 50% of its initial value, or until the slope of the absorbance versus time plot reaches a constant value.

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

$$A = \varepsilon\, c\, \ell \qquad (16)$$

(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 Br_2 with time, $d[Br_2]/dt = dc/dt$, is given by the expression

$$dc/dt = (1/\varepsilon\ell)\, dA/dt \qquad (17)$$

Since ε for Br_2 is given above, equation (17) can be used to find the rate of change in bromine concentration with time. By analyzing the experimental data as suggested by equation (12), determine the order of the reaction with respect to hydrogen ion and acetone. Finally, 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 rate orders to the nearest integer values. Note 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 Br_2, and because we have chosen to work under conditions where $[H^+]$, $[CH_3COCH_3] \gg [Br_2]$. 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	0.02 M Br_2	1.0 M HCl	4.0 M acetone
1	10 mL	10 mL	10 mL
2	10 mL	15 mL	10 mL
3	10 mL	20 mL	10 mL
4	10 mL	25 mL	10 mL
5	10 mL	10 mL	15 mL
6	10 mL	10 mL	20 mL
7	10 mL	10 mL	25 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) You do not need to compare your experimental results (reaction orders and rate constant) with literature values.

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.

Revised 1/2017

Kinetics of the mutarotation reaction of glucose

Introduction

Optical isomers

Most simple chemical compounds can be superimposed on their mirror image. For example, Figure 1 gives a molecule of 2-propanol and the mirror image of the molecule. The mirror image can be superimposed on the original molecule and is therefore not distinguishable, but is in fact the same molecule.

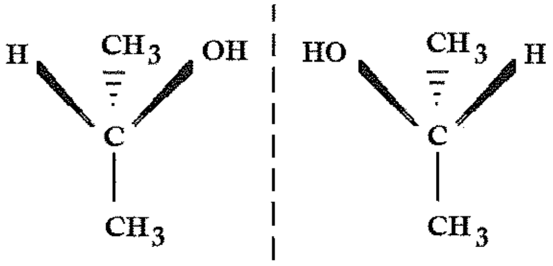


Figure 1. 2-propanol and its mirror image.

There is, however, a class of molecules that cannot be superimposed on their mirror image. A simple example of such a molecule is 2-butanol, shown in Figure 2. The two molecules of 2-butanol in the figure are mirror images of one another, just as was the case in Figure 1. However, unlike the mirror images in Figure 1, the 2-butanol molecule and its mirror image cannot be superimposed on one another, and therefore represent distinct molecules. Molecules that cannot be superimposed on their mirror image are called optically active molecules, for reasons discussed below, with the non-superimposable forms of the molecules called optical isomers.

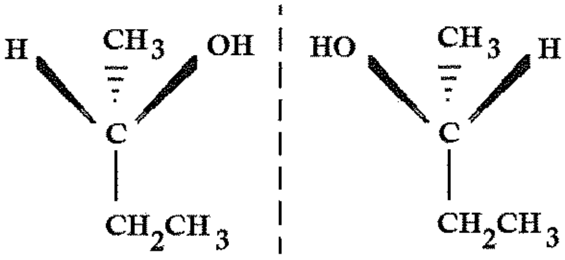


Figure 2. 2-butanol and its mirror image.

Additional information concerning optically active molecules and optical isomers can be found in reference [1] or most other standard organic texts.

Rotation of light

The physical property that distinguishes an optically active molecule from an optically inactive molecule is the way in which the molecule interacts with polarized light. Polarized light is light where the electromagnetic oscillations have been oriented in a particular plane perpendicular to the direction in which the light is moving. Polarized light can be produced by reflection of light from a surface or by passing light through a crystal or oriented polymeric film. When polarized light passes through a solution containing only optically inactive molecules, no change in the plane of polarization of the light is observed. However, if an optically active molecule is present in the solution, the plane of polarization of the light will be rotated either to the right (positive, D, or dextrorotatory) or to the left (negative, L, or levorotatory). The angle of rotation of the plane of polarization of the light is given the symbol α. Some of the properties of polarized light and its interaction with optically active molecules are discussed in reference [2].

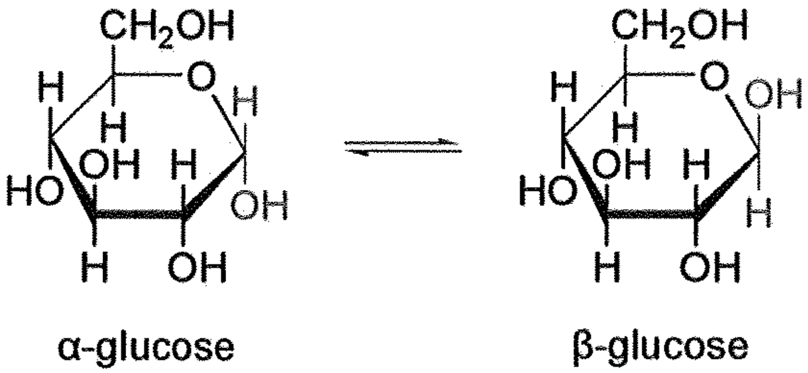
The amount of rotation that a plane polarized beam of light undergoes when passing through a solution containing optically active molecules depends on many factors, including the concentration of optically active molecules in solution, the wavelength of the polarized light, the pathlength, the temperature, and the solvent. Because of this, a reference condition is needed for reporting optical activity. The specific rotation of an optically active compound, given the symbol $[\alpha]_D^T$, is defined as the observed rotation for a 1 g/mL concentration of the pure optically active compound in a 10 cm polarimeter cell, at a fixed temperature T, using polarized light from the D line of a sodium emission lamp (actually a closely spaced doublet line occurring at 589.3 nm, corresponding to the $^2P \rightarrow {}^2S$ electronic transition). The relationship between α_{obsd}, the rotation observed for a particular concentration and pathlength, and $[\alpha]_D^T$, the specific rotation of the compound is

$$[\alpha]_D^T = 10(\alpha_{obsd})/c\ell \qquad (1)$$

where c is the concentration of the optically active compound (in g/mL) and ℓ is the pathlength of the polarimeter cell (in cm).

The mutarotation reaction

Glucose is a monosaccharide, a sugar with the chemical formula $C_6H_{12}O_6$. In water, glucose exists in two cyclic forms (which themselves have non-superimposable forms that are their optical isomers), as shown in Figure 3. These two forms of glucose are not mirror images of one another because there is more than one optically active site in the molecule. As it happens, both of these molecules are dextrorotatory.



$[\alpha]_D^{25} = +\ 112.0$ ° $\qquad [\alpha]_D^{25} = +\ 18.7$ °

Figure 3. The α and β isomers of D-glucose.

The mutarotation reaction occurs by protonation of the ring oxygen atom followed by formation of the linear, or aldehydic, form of the sugar. When the cyclic form of the sugar is regenerated either the α or the β configuration can occur. Thus one cyclic form of glucose may be converted to the other cyclic form of glucose. Whether we begin with the α or the β form of glucose, the aldehydic intermediate is the same. The mutarotation reaction thus generates an equilibrium concentration of α and β forms from any initial nonequilibrium concentration of starting material.

Kinetics

The mutarotation reaction is a kinetic system with the form

$$A \leftrightarrow B \qquad (2)$$

where

$A = \alpha$-D (+) glucose
$B = \beta$-D (+) glucose
k_1 = rate constant for conversion of A into B
k_{-1} = rate constant for conversion of B into A

The rate law in differential form is then

$$d[A]/dt = - k_1 [A] + k_{-1} [B] \qquad (3)$$

where d[A]/dt is the rate of change in the concentration of A with time. Note that at equilibrium (with equilibrium quantities labeled eq)

$$(d[A]/dt)_{eq} = 0 = - k_1 [A]_{eq} + k_{-1} [B]_{eq} \qquad (4)$$

or

$$[B]_{eq}/[A]_{eq} = K_{eq} = k_1/k_{-1} \qquad (5)$$

which gives a simple relationship between the equilibrium constant for the reaction and the rate constants for the reaction.

Returning to equation (3), we may integrate to obtain the time dependence of the concentration of A. The result [3] is

$$([A]_t - [A]_{eq})/([A]_0 - [A]_{eq}) = \exp[- (k_1 + k_{-1}) t] \qquad (6)$$

or

$$\ln\{([A]_t - [A]_{eq})/([A]_0 - [A]_{eq})\} = - (k_1 + k_{-1})t = - k_{obsd}t \qquad (7)$$

where we have defined $[A]_0$ as the concentration of A at some convenient starting time t = 0 (which, because the reaction is first order, is arbitrary), $[A]_{eq}$ as the concentration of A at equilibrium, and k_{odsd}, the observed rate constant, as the sum of the forward and reverse rate constants for the reaction (that is, $k_{obsd} = k_1 + k_{-1}$). Note that the rate at which the system approaches equilibrium is determined by the sum of k_1 and k_{-1}.

The optical rotation of a solution containing α-D (+) glucose and β-D (+) glucose is directly proportional to the concentration of the α-isomer for a fixed path length and total glucose concentration. Equation (7) can therefore be rewritten as

$$\ln\{(\alpha_0 - \alpha_{eq})/(\alpha_t - \alpha_{eq})\} = k_{obsd}t \qquad (8)$$

where α_t is the observed rotation of the solution at time t, α_0 is the observed rotation at t = 0, and α_{eq} is the rotation observed when the system has reached equilibrium. Notice that we do not need to convert the observed rotation of the solution to a specific rotation, nor do we need to know the constant of proportionality that relates α_t to $[A]_t$.

You should also record the temperature of the room for the day that data is taken. While the temperature will not be used in your calculations, differences in temperature on different days can affect the rate constant (and, to a lesser extent, the equilibrium constant) for the reaction.

Lab report

Your laboratory report should include the following:

1) A table containing your raw data (rotation vs time for each solution, including the values for α_{eq}).

2) A plot of $\ln\{(\alpha_0 - \alpha_{eq})/(\alpha_t - \alpha_{eq})\}$ vs t for each solution, and an explanation of how these plots were used to determine the value for k_{obsd} for each solution.

3) The experimental values for K_{eq} for each solution. You will have to derive an equation for finding K_{eq} based on the information you have available to you.

4) The average value for K_{eq}, and the 95% confidence limits for that value. This can be found by taking an average of the four experimental values for K_{eq}. Doing this assumes that the value for K_{eq} is independent of $[H^+]$. Is that a reasonable assumption? Why or why not?

5) A discussion of the effect of hydrogen ion concentration on the value of k_{obsd}, including a determination of experimental values for the neutral (k_n) and acid catalyzed (k_a) rate constants, along with an appropriate plot of the data.

6) You do not need to compare your experimental results (values for k_n, k_a, and K_{eq}) with literature values.

References

1. T. W. G. Solomons, C. B. Fryhle, S. A. Snyder Organic Chemistry, Twelth Edition, (Wiley, New York, 2016) pp. 193-213.

2. C. W. Garland, J. W. Nibler, D. P. Shoemaker Experiments in Physical Chemistry, Eighth Edition, (McGraw-Hill, Philadelphia, 2009), pp. 611-612.

3. S. W. Benson, Foundations of Chemical Kinetics, (McGraw-Hill, New York, 1960), pp. 27-29.

4. If a different concentration of the concentrated PCA solution is used, the solutions should be still be prepared as in the table below, and the concentrations adjusted accordingly. For example, if 60% PCA were used, it would have a concentration of 0.199 M.

Acknowledgements: Figures 1-4 are taken from T. W. G. Solomons, Organic Chemistry, Sixth Edition, (Wiley, New York, 1996).

Revised 1/2017