

application note

Kinetics Rate Law Investigations by UV-Visible Spectrometry

*Lindsay Moore and John Bishop
GBC Scientific Equipment Pty Ltd.*

Introduction

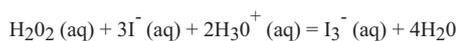
Rates of chemical reactions determine how quickly a reaction mixture will reach its equilibrium state. The rate can depend upon a number of factors which can be controlled such as temperature, pH, pressure and the presence of a catalyst. For example, in an industrial process it might be economical for reactions to proceed very rapidly; but not so rapidly as to produce an explosion. By contrast, in a biological process it may be appropriate for a reaction to proceed slowly and to be switched on and off at the demand of some specific activity.

The basic data of chemical kinetics is the concentrations of the reactants and products as a function of time. The method selected for monitoring the concentrations depends upon the nature of the species involved and the rate of reaction. A number of general methods are available for monitoring the concentrations including pressure changes in gas phase reactions, polarimetry when the optical activity of a mixture changes, conductivity/electrochemical methods for redox reactions and spectroscopic methods when the products or reactants absorb UV or visible light.

Chemical reactions are classified on a kinetics basis by reaction order i.e., zero, **first** and second order, depending on how the reaction rate is influenced by the concentration of the reactants under a given set of conditions. For example, **first** order reactions are those

which proceed at a rate directly proportional to the concentration of one reactant.

In this study the effect of reagent concentrations on the rate of oxidation of iodide by hydrogen peroxide in acid solution,



has been studied to determine the form of the rate law. The reaction has been monitored via the formation of tri-iodide (I_3^-) using a UV/Visible spectrophotometer.

Experimental

Instrument

A GBC 914 double beam UV/Visible spectrometer running KINETICS application software was used in this study. The instrument was fitted with a water thermostatted 7 x 7 carousel cell holder accessory combined with a Neslab Exacal EX-110 constant temperature water recirculator.

The KINETICS software allows collection of either single- or multi-wavelength data. Post-run data analysis of either product formation or reagent consumption includes zero, first and second order rate determinations as well as a versatile tangent ruler function. The software also provides a facility to plot initial reaction rate against a user-defined run variable such as pH, temperature or reagent concentrations.

Reagents/Materials

(a) A 0.8M hydrogen peroxide solution was prepared by diluting 34.9 mL hydrogen peroxide (Selby's Scientific 130 vol) to 500 mL with water.

(b) A 0.025M potassium iodide solution was prepared by dissolving 2.075 g potassium iodide (Ajax Chemicals Univar AR) in 500 mL water.

(c) A 0.36M sulphuric acid solution was prepared by diluting 19.1 mL concentrated H_2SO_4 (Malinckrodt AR) to 1000 mL with water.

Rate Measurement

A series of experiments were performed in which the concentration of one of the reagents was varied. Reaction mixtures of 100 mL were prepared in which the volume of the particular reagent and volume of water was varied. The volumes are given below.

(1) Effect of peroxide

0.5, 1.0 and 2.0 mL 0.08M H_2O_2
35 mL 0.36M H_2SO_4
10 mL 0.025M KI
 H_2O to 100 mL

(2) Effect of iodide

2.0 mL 0.08M H_2O_2
35 mL 0.36M H_2SO_4
5, 10 and 20 mL 0.025M KI
 H_2O to 100 mL

(3) Effect of acid

2.0 mL 0.08M H_2O_2
17.5, 35 and 70 mL 0.36M H_2SO_4
10 mL 0.025M KI
 H_2O to 100 mL

Approximately 3 mL of the reaction mixture was transferred to a cuvette and the rate of reaction monitored via the formation of the tri-iodide (I_3^-) at 353 nm. The instrument operating conditions are given in Table 1.

Table 1. Instrument operating parameters

Measurement Type	Single Wavelength
Measurement Wavelength	353 nm
Scan Duration	300 s
Cycle Time	2 s
Integration Time	1 s
Lag Time	2 s

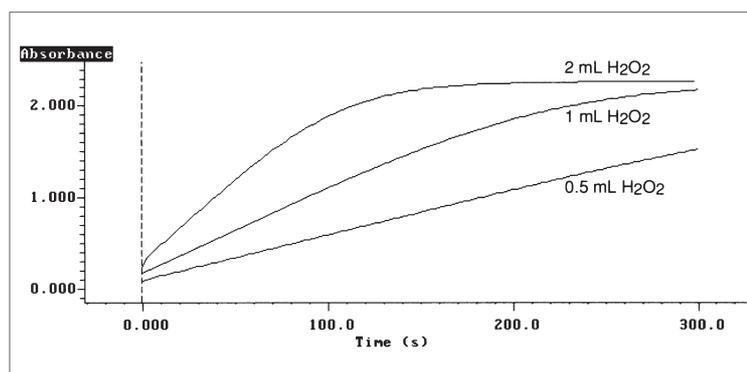
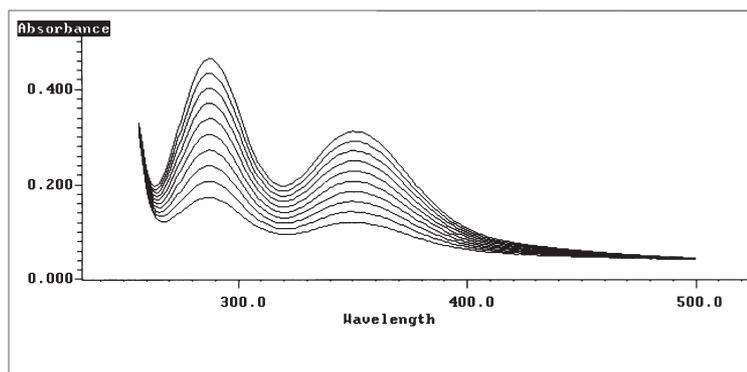


Fig. 1. (top pic) Series of wavelength scans as a function of time for one of the reaction mixtures

Fig. 2. (lower pic) Time scans showing the effect of peroxide concentration on absorbance at 353 nm.

Results

A series of preliminary wavelength scans as a function of time was performed on one of the reaction mixtures to ascertain the measurement wavelength for the kinetics studies. These scans are shown in Figure 1. The scans show two absorbance peaks at 288 and 353 nm which can be attributed to the formation of the tri-iodide species. The 353 nm absorbance peak was used to study the kinetics of the reaction system since a literature value for the extinction coefficient at this wavelength was available. The extinction coefficient for tri-iodide at 353 nm is $26,400 \text{ dm}^3\text{cm}^{-1}\text{mol}^{-1}$.

Figure 2 shows the raw absorbance at 353 nm versus time data for the three samples in which the concentration of peroxide was varied.

Rate constants and initial reaction rates (or velocities) can be determined from experimental data by transforming the data to a form in which the transformed data versus time is linear. In the simplest case, zero order, the rate is independent of concentrations of reagents and so a plot of product concentration versus time is linear with the slope of the plot corresponding to the reaction rate. Concentrations are obtained simply by multiplying the absorbance data by a concentration factor. The concentration factor is simply the reciprocal of the extinction coefficient if using a standard 1 cm pathlength cell. In first order reactions, a logarithmic transform must be performed on the data. The data is transformed to $\ln([A]_t/[A]_0)$ where $[A]_t$ is the reagent concentration at time t and $[A]_0$ is the initial reagent concentration. The slope of the plot of the logarithmic transform versus time corresponds to the rate constant, k . In second order reactions, a plot of $1/[A]_t$ versus time is linear and the slope is the second order rate constant. The GBC 914/916/918/920 KINETICS software performs zero, first and second order transforms and rate constant determinations.

In this study, zero order transformations have been performed on the absorbance data, and only the initial absorbance-time data used in the calculations. The initial stages of most reactions can be considered as zero order. The results of the initial velocity determinations for all samples are given in Table 2.

Table 2. Results of the initial velocity determinations for all samples.

Calculated Rate Constants		
Results File Name: RATE_1		
Method File Name: IODINE		
Reaction Order: Zero Order		
Measurement Wavelength: 353.0 nm		
Sample Label	Velocity (/sec) $\times 10^{-6}$	V_o Error $\times 10^{-6}$
0.5 mL peroxide	0.1992	0.0019
1.0 mL peroxide	0.3581	0.0009
2.0 mL peroxide	0.7350	0.0069
Calculated Rate Constants		
Results File Name: RATE_2		
Method File Name: IODINE		
Reaction Order: Zero Order		
Measurement Wavelength: 353.0 nm		
Sample Label	Velocity (/sec) $\times 10^{-6}$	V_o Error $\times 10^{-6}$
5 mL KI	0.1755	0.0003
10 mL KI	0.3317	0.0005
20 mL KI	0.6951	0.0026
Calculated Rate Constants		
Results File Name: RATE_3		
Method File Name: IODINE		
Reaction Order: Zero Order		
Measurement Wavelength: 353.0 nm		
Sample Label	Velocity (/sec) $\times 10^{-6}$	V_o Error $\times 10^{-6}$
0.0 mL acid	0.0830	0.0001
17.5 mL acid	0.2340	0.0010
35 mL acid	0.3534	0.0032
70.0 mL acid	0.6204	0.0001

The rate law is an equation that expresses the dependence of the rate of a chemical reaction on the concentrations of reagents.

Rate laws can be determined from the measurement of the initial reaction rate or velocity. If the rate is proportional to the concentration of the reagent then a plot of initial velocity (V_0) versus concentration will be linear. The GBC 914/916/918/920 KINETICS software allows the user to plot the initial velocity versus a run variable, for example concentration of a reagent. Figure 3 shows plots of initial velocity versus reagent volume for the three reagents, peroxide, iodide and acid. It is clear from the plots that the main relationships involved are:

- the initial rate increases in proportion to the concentration of peroxide.
- the initial rate increases in proportion to the concentration of iodide.
- the initial rate increases linearly with acid concentration but at zero concentration the initial rate is not zero.

These observations imply that the experimental relationship between the initial reaction rate and the concentrations of reagents has the form

$$\text{Rate} = x [\text{H}_2\text{O}_2] [\text{I}^-] (y + [\text{H}^+])$$

which can be written in the more common chemical kinetics form

$$\text{Rate} = k [\text{H}_2\text{O}_2] [\text{I}^-] + k' [\text{H}_2\text{O}_2] [\text{I}^-] [\text{H}^+]$$

where k and k' are the rate constants or coefficients.

Hence the rate law consists of two terms. The first term is first order with respect to hydrogen peroxide and iodide concentration, and zero order with respect to acid concentration, and is thus second order overall. The second term is first order with respect to the concentration of all reagents and is thus third order overall. Finally, the rate law indicates that the acid acts as a catalyst in the oxidation of iodide by hydrogen peroxide.

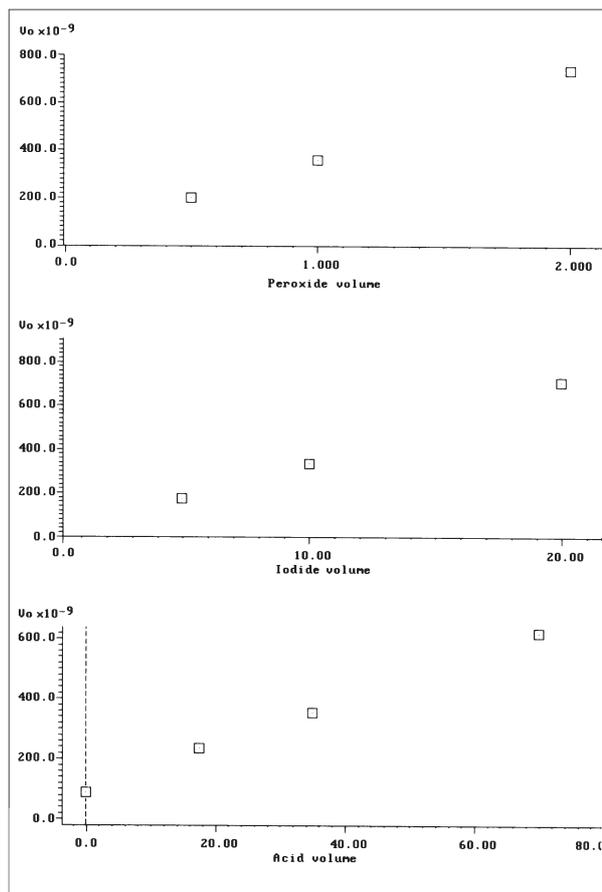


Fig. 3. Plots of initial velocity, V_0 , against peroxide, iodide and acid volumes.

Conclusions

A GBC 914 UV/Visible spectrophotometer running KINETICS software has been used to determine the form of the rate law for the oxidation of iodide by hydrogen peroxide. The GBC 914/916/918/920 range of double beam UV/Visible spectrophotometers provides a simple and versatile means of studying kinetic reactions. The KINETICS software gives complete flexibility in data handling and storage. In this study initial velocities have been determined using the software's built-in calculations facility, and plotted as a function of reagent volume to ascertain the form of the rate law.