Kinetics of Dye Bleaching

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Objective:
Examine the ***kinetics*** of the reactions by which two structurally similar dyes are bleached

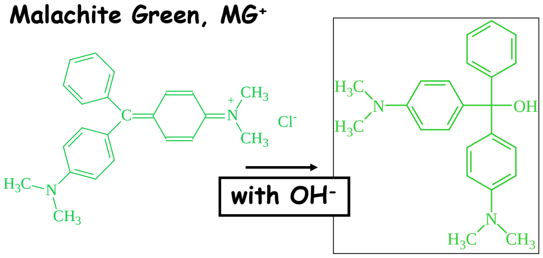
Concepts:
Reaction Rate — Rate Law — Order of reaction
Specific Rate — Beer's Law
Linear Graphs from non-linear relationships

Techniques:
Using Spectrophotometer — Isolation Experiment

Apparatus:
Spectronic 20 — Constant Temperature Bath
Timer

This exercise explores the time dependence of the reactions of the dye:

Malachite Green, MG^+



To form the corresponding alcohols, **MGOH** which is **colorless**

We write the reaction as

$$MG^+ + OH^- \rightarrow MGOH$$

Rate law for the reaction is

$$rate = -\frac{d[MG^+]}{dt} = k\,[OH^-]^n\,[MG^+]^m$$

k = ***specific rate*** of the reaction

m = ***order of the reaction*** with respect to MG^+

n = ***order of the reaction*** with respect to OH^-

Our **objective** is to determine **k**, **n** and **m**

Since the reactant, MG^+ is *colored* but neither OH^- nor the product, **MGOH**, is (i.e., OH^- *bleaches* the dye)

We can follow the ***concentration*** of MG^+ as the reaction proceeds using the **Absorbance** of light and

Beer's Law

$$A = e\,c$$

Where, as usual,
e will be the slope of the Beer's Law plot for the dye. ($e = \varepsilon\,d$)

$$rate = -\frac{d[MG^+]}{dt} = k\,[OH^-]^n\,[MG^+]^m$$

If $[OH^-]$ didn't change, the rate law would simplify to one involving only ***one*** changing concentration, $[MG^+]$

$$rate = -\frac{d[MG^+]}{dt} = q\,[MG^+]^m$$

where $q = k\,[OH^-]^n$

We can accomplish this experimentally by
Using a **large** (excess), **known** $[OH^-]$

Then, $[OH^-]$ will **not change significantly** during the course of the reaction -- an "***Isolation Experiment***"

To keep things simple, in this exercise, we will limit the possible values of both **m and n to** either 1 or 2

For these two cases, calculus provides an expression for the way in which **[MG⁺]** will vary with time, namely:

m = 1 $\quad - d[MG^+] / dt = q [MG^+]^1$

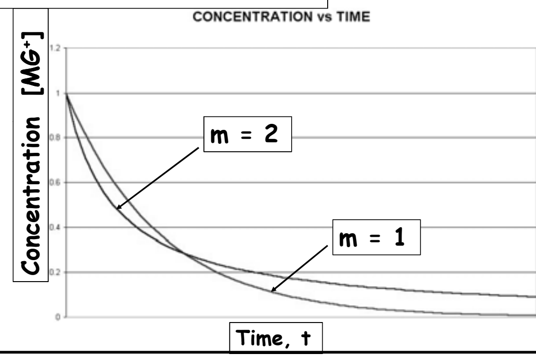
$$\frac{dy}{dt} = q\,y \qquad [MG^+] = A\,e^{-qt}$$

m = 2 $\quad - d[MG^+] / dt = q [MG^+]^2$

$$\frac{dy}{dt} = q\,y^2 \qquad \frac{1}{[MG^+]} = B + qt$$

where **A, B** are constants fixed by **[MG⁺]** at t = 0.

If we measure **[MG⁺]** at a sequence of times, we should be able to tell the value of **m** by plotting the ***concentration***



But, we can produce **linear** plots *vs* time

for m = 1

$$[MG^+] = [MG^+]_0\,e^{-qt}$$

taking the natural logarithm of each side produces:

$$\ln [MG^+] = \ln [MG^+]_0 - q\,t$$

for m = 2
We have

$$\frac{1}{[MG^+]} = \frac{1}{[MG^+]_0} + q\,t$$

If the plot of **ln [MG⁺]** is **linear** with time, the reaction is **first** order with respect to **MG⁺**
i.e., **m = 1**

If the plot of **(1 / [MG⁺])** is **linear** with time, the reaction is **second** order with respect to **MG⁺**
i.e., **m = 2**

This is how we determine **m**

In either case, the slope of the line is $q = k [OH^-]^n$

But we actually measure ***absorbance***, not ***concentration***

REMEMBER!

In *pre-lab problem 3*, you willshow that the slope of the second order (**m = 2)** plot of absorbance *vs* time involves the Beer's Law constant for the dye, **e**.

$$\frac{1}{Abs} = \frac{1}{Abs_0} + q\,t / e$$

Having determined **m**, how do we determine **n**, the ***order of the reaction with respect to OH⁻*** ?
Study reaction at two different values of **[OH⁻]**, c_1 and c_2, insuring that they are both in large excess over the concentration of **MG⁺.**

This gives us two slopes q_1 and q_2, whose different values depend on the two OH⁻ concentrations by

m = 1

$$q = k [OH^-]^n$$

$$\frac{q_1}{q_2} = \frac{k [OH^-]^n / e}{k [OH^-]^n / e} = \frac{k\,c_1^n / e}{k\,c_2^n / e}$$

$$\log q_1 / q_2 = c_1^n / c_2^n = og\,(c_1 / c_2)^n$$

Having determined **m**, how do we determine **n**, the ***order of the reaction with respect to OH⁻*** ? Study reaction at two different values of **[OH^-]**, c_1 and c_2, insuring that they are both in large excess over the concentration of ***MG^+***.

This gives us two slopes q_1 and q_2, whose different values depend on the two OH^- concentrations by

$$\frac{q_1}{q_2} \qquad \frac{k\,[\,OH^-\,]^n}{k\,[\,OH^-\,]^n} = \frac{k\,c_1^{\,n}}{k\,c_2^{\,n}}$$

$$\log q_1 / q_2 \;=\; c_1^{\,n} / c_2^{\,n} \;=\; og\,(c_1 / c_2)^n$$

$$\log(q_1 / q_2) = n \log(c_1 / c_2)$$

$$n = \frac{\log(q_1 / q_2)}{\log(c_1 / c_2)}$$

q_1 and q_2 are known from the slopes of our graphs

c_1 and c_2 from the way we made up the solutions.

When we solve $n = \log(q_1/q_2) / \log(c_1/c_2)$ for **n**, we will consider only the **integer** solutions: **1 or 2**

This is how we determine n

A simpler way of looking at the argument used to determine **n** is:

In the exercise, **[OH^-]** in **run 2** is exactly $\frac{1}{2}$ of **[OH^-]** in **run 1**

Since the slope of each run depends on **[OH^-]^n**,

if <u>$n = 1$</u>

slope in **run 2** should be $\left(\frac{1}{2}\right)^1 = \frac{1}{2}$ of slope in **run 1**

i.e., $q_2 = \frac{1}{2}\,q_1$

if <u>$n = 2$</u>

slope in **run 2** should be $\left(\frac{1}{2}\right)^2 = \frac{1}{4}$ of slope in **run 1**

i.e., $q_2 = \frac{1}{4}\,q_1$

Having determined both **m** and **n**, we can now go back and calculate **k**, the ***specific rate***.

If m = 1

$q_1 = k\,[\,OH^-\,]^n$

$q_2 = k\,[\,OH^-\,]^n$

If m = 2

$q_1 = k\,[\,OH^-\,]^n / e$

$q_2 = k\,[\,OH^-\,]^n / e$

where **e** is the Beer's Law constant for the dye

In either case, report the ***average*** of the two values

<u>PROCEDURE</u>

WORK IN PAIRS

1.) Prepare ***appropriate dilutions*** of **MG^+** and NaOH stock solutions

2.) Permit solutions to come to **room temperature**

Measure absorbance of the dye solution as in **procedure 3b**

Blank should be NaOH – use water instead

3.) Start timer, combine, and mix solutions

<u>ALL AT THE SAME TIME (t=0)</u>

Don't stop the timer!

<u>WAVELENGTH ADJUSTMENT</u>: sets *wavelength* (color)

<u>ZERO ADJUSTMENT</u>: sets *0% transmittance* – calibrates detector. Needs *only Periodic* checking after warm-up

<u>LIGHT CONTROL</u>: sets *100 % transmittance*. Needs readjustment before *every measurement* of a sample. (Using BLANK)

PROCEDURE (cont'd)

4.) Make an absorbance measurement as soon as possible
appropriate time intervals as instructed (~60 sec, ~120 sec, etc),
Record absorbance & ***total elapsed*** **time**

5.) **Plot data** on lab computer and decide on **m**, the order of the reaction with respect to **MG^+**

6.) From the slope of the plot, **determine the *apparent* specfic rate** constant **q**

This slope includes the term **$[\ OH^-\ ]^n$**

i.e., $q = k\,[\ OH^-\ ]^n$ and **e** if **m = 2**

7.) Repeat Steps 1-6 using **different $[\ OH^-\ ]$**

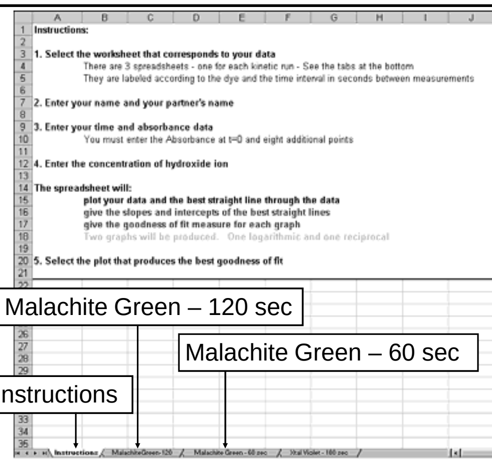
8.) **Plot new data** appropriately *vs* time,
Use the ***same function*** (i.e., ***ln*** or **1/[Dye]**)
that produced linear plot *in* ***Run 1***

9.) From the 2 sets of data, determine **n**, and the specific rate constant **k**

Note: The cuvettes may become slightly stained by the dyes. If so, they can be cleaned by rinsing with 2-3 mL of 95% ethanol

It will be helpful to have a watch with a second hand for this exercise.

We will omit the part of the exercise dealing with Crystal Violet


Instructions:

1. Select the worksheet that corresponds to your data
There are 3 spreadsheets - one for each kinetic run - See the tabs at the bottom
They are labeled according to the dye and the time interval in seconds between measurements

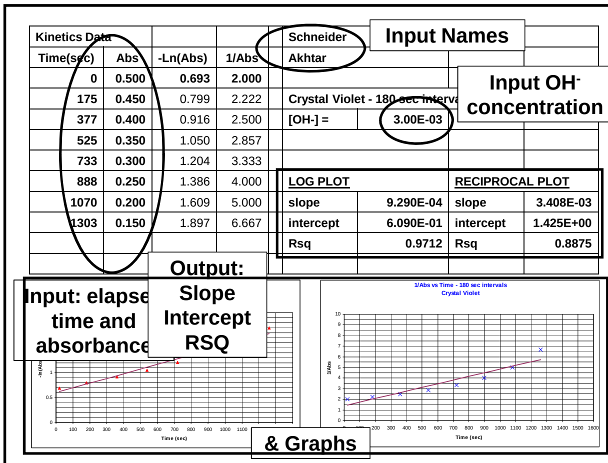
2. Enter your name and your partner's name

3. Enter your time and absorbance data
You must enter the Absorbance at t=0 and eight additional points

4. Enter the concentration of hydroxide ion

The spreadsheet will:
plot your data and the best straight line through the data
give the slopes and intercepts of the best straight lines
give the goodness of fit measure for each graph
Two graphs will be produced. One logarithmic and one reciprocal

5. Select the plot that produces the best goodness of fit



Kinetics Data				Schneider			
Time(sec)	Abs	-Ln(Abs)	1/Abs	Akhtar			
0	0.500	0.693	2.000				
175	0.450	0.799	2.222	Crystal Violet - 180 sec interva			
377	0.400	0.916	2.500	[OH-] =	3.00E-03		
525	0.350	1.050	2.857				
733	0.300	1.204	3.333				
888	0.250	1.386	4.000	LOG PLOT		RECIPROCAL PLOT	
1070	0.200	1.609	5.000	slope	9.290E-04	slope	3.408E-03
1303	0.150	1.897	6.667	intercept	6.090E-01	intercept	1.425E+00
				Rsq	0.9712	Rsq	0.8875

Time (sec)	Abs	-ln(Abs)	1/Abs
10	0.500	0.693	2.000
175	0.450	0.799	2.222
377	0.400	0.916	2.500
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Spreadsheets require exactly 8 entries

In order of increasing time

Note that times are the ***total elapsed seconds***