

KINETICS OF THE ACID-CATALYZED HYDROLYSIS OF GLYCIDOL

Reference: B. Spencer and R.N. Zare, *J. Chem. Ed.* **65**, 835 (1988).

LASER SAFETY

One must be cautious using any laser system. **NEVER LOOK INTO THE BEAM OF ANY LASER! REFLECTIONS FROM POLISHED SURFACES MAY BE AS DANGEROUS AS THE BEAM ITSELF!** Always be aware of the beam path and those around you when adjusting the path. Appropriate laser goggles must always be worn.

Introduction

Most of the kinetics experiments you are familiar with involve obvious signs of reaction, for example, the iodine clock reactions change color. Other reactions may produce changes in temperature or phase. These systems are merely a convenient subset of reactions, chosen for ease of operation in a teaching laboratory environment. The majority of chemical reactions produce no obvious sign of change and require some sophisticated techniques to follow the course of the chemistry. However, in many instances, the reactant and product have a different index of refraction, n . The index of refraction is the cause of light "bending" as it passes from air into another medium (recall the description of the quartz beamsplitter in an earlier lab). You have probably seen such an effect as a light beam passes into a tank of water. In general, the angle at which the light beam is incident (from air, $n = 1$) on the sample, i , and the angle of refraction, r , are related by Snell's Law:

$$n = \sin i / \sin r. \quad (1)$$

Snell's Law, as written in equation (1) assumes special measurement conditions, which are difficult to maintain. Instead, we shall employ a simple test tube as a sample cell. The mathematics describing refraction through a curved surface are much more complicated, but we are only concerned with the final results. The situation is pictured below in Figure 1, where θ is the beam displacement angle and i and r have already been defined. In this example, i and r are related by Equation (2)

$$\theta = 4r - 2i \quad (2)$$

and the angle of refraction is controlled by the index of refraction of the medium in the sample cell:

$$r = \sin^{-1} [(4 - n^2)/3n^2]^{1/2}$$

The quantity measured as a function of time is the beam displacement, Y:

$$Y = \tan\{4 \sin^{-1} [(4 - n^2)/3n^2]^{1/2} - 2i\}$$

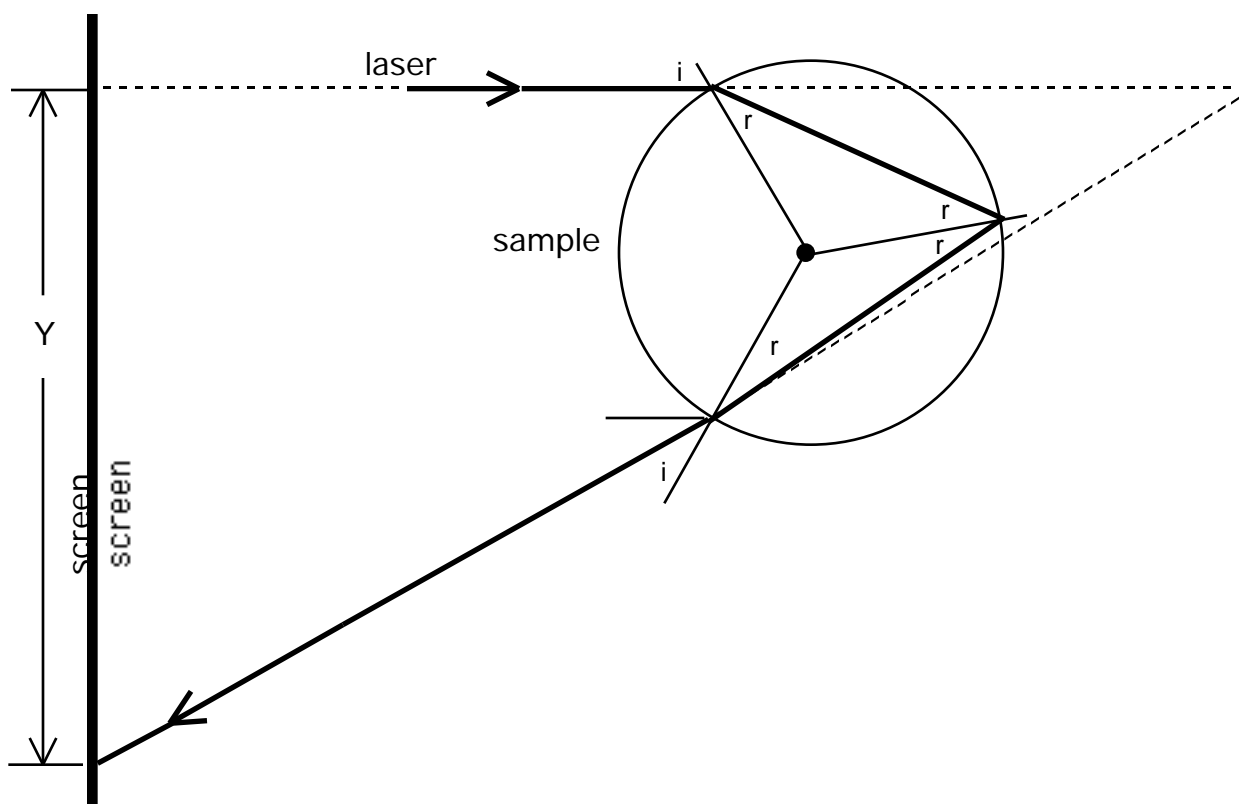


Figure 1. Schematic of the arrangement using a test tube sample holder.

As the reaction proceeds, the index of refraction of the solution continuously changes from that of the reactants to that of the products and the refracted beam moves in concert across the screen used to visualize it.

The specific chemistry to be studied is the *acid-catalyzed* hydrolysis of 2,3-epoxy-1-propanol, also known by the trivial name glycidol, into the more familiar molecule glycerol. The overall chemistry is shown pictorially in Figure 2.

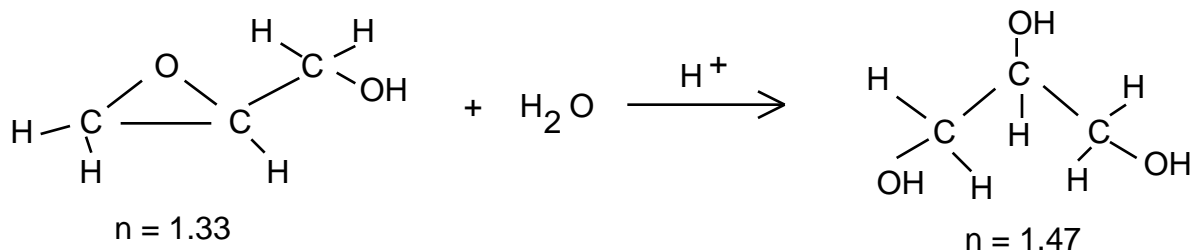


Figure 2. The acid-catalyzed hydrolysis of glycidol to glycerol.

As indicated the refractive index undergoes a substantial change during the course of the reaction and the process is readily followed by the technique described above.

Experimental

This experiment is set up as a collaborative effort. The four sets of reaction conditions are noted below in Table I. You and your lab partner will be assigned one of these sets (or, if necessary a unique set) by the TA in the lab. In order to complete the lab report, you will need the results obtained by the other student groups performing the experiment on your lab day. Before you leave the lab, be sure to give a copy of your kinetics results (beam deflection vs. time at your assigned reaction temperature) to your TA. You will receive all sets of data by BlitzMail in the evening after you have finished the lab.

Table I

Reaction Conditions		
Glycidol Concentration	[HClO ₄], M	T, °C
30%	6	30
30%	6	40
30%	6	50
30%	3	50

Note that the temperature refers to the bath temperature. The actual reaction temperature will be a few degrees cooler.

Glycidol is toxic and an irritant. You will find a solution of 30% glycidol in water already prepared, placed in a test tube and thermostatted in a constant temperature bath in the lab. Clamp the cell in the holder above the magnetic stirrer already mounted in place on your laser bench. Remove the cap from the tube and insert the thermostating finger (to maintain temperature during the course of the reaction) and the thermocouple

(a pair of dissimilar metals that produces a voltage proportional to the temperature). Turn on the stirrer and the water flow to the thermostating finger. The experimental setup is diagrammed in Figure 3. Allow the temperature to stabilize for approximately 3-5 minutes during which time you can turn on the laser and check to be sure that the refracted beam is focused on the observation screen such that the edge of the laser spot is at zero. Once you begin taking data, do not move the screen. We are employing the change in beam position from the unreacted state rather than the quantity called Y above. After noting the temperature, add **15 μ L** of the appropriate concentration of HClO_4 and start the digital timer. Obtain readings at approximately 5 minute intervals until the deflection stops changing or until you have collected 8-10 data points. Check to be sure that the temperature remains relatively constant and record the temperature with each deflection measurement. Little heat is generated under these conditions and we do not anticipate that any significant change in T will be detected.

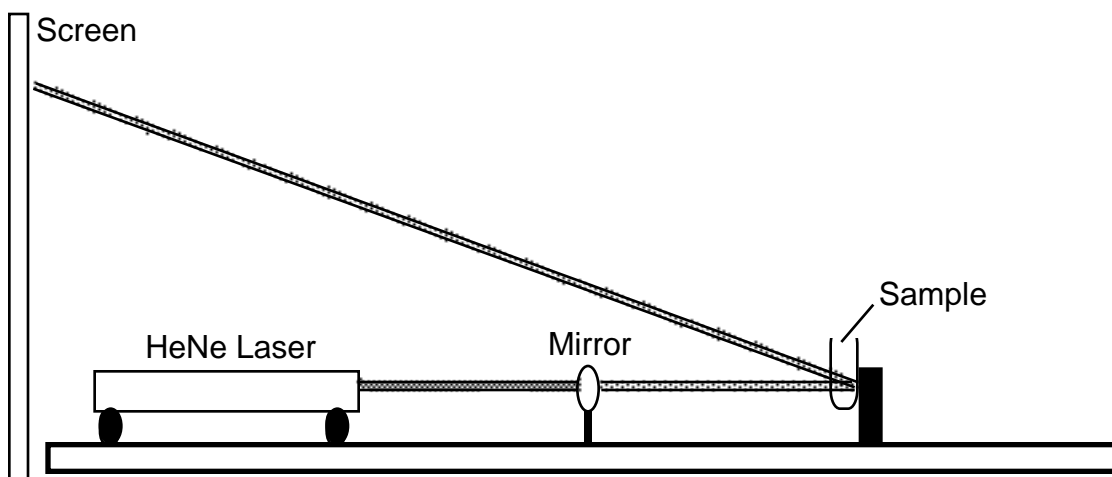


Figure 3. Experimental apparatus.

Analysis and Write-up

Construct kinetic plots of laser beam displacement as a function of time for each of the four kinetic runs (see Appendix A for a helpful discussion). From these plots, determine the rate constant for the hydrolysis reaction as a function of temperature and acid concentration. In the case of temperature, use the average value during the course of the run.

You have only two data points, but determine the order of the dependence of the rate constant on HClO_4 concentration.

Estimate the activation energy for this reaction using an Arrhenius plot. The program LEAST SQUARES, available on the PUBLIC FILE SERVER and may be of use to you (if you have a Mac) in your calculations. Microsoft Excel may also be used to obtain graph and best fit line.

Questions (to be handed in with lab report)

- (1) Assume that the reaction begins with no glycerol present and goes to completion. What would be the net change in displacement if the angle of incidence is 20° ?
- (2) The experimental procedure notes that there is little change in temperature during the course of this reaction. Use your experimentally determined value of activation energy to estimate the maximum uncertainty in your rate constant (just your particular reaction conditions). To do this, calculate the ratio of the predicted rate constant at the extremes of your measured temperature range to the rate constant at the average temperature during the course of the reaction.
- (3) Write a plausible rate determining step for the mechanism of this reaction based on your experimental observations (at least propose the reactants in such a step!).

Appendix A

Kinetics measurements by monitoring a property that depends on reactants and products

We generally talk about kinetics experiments as though we have data consisting of the actual concentration of a reactant or a product as a function of time. We may then plot the concentrations in the proper format (ln conc. vs. t, 1/conc. vs. t, etc) and determine the order and rate constant for the reaction. While such a collection of data is useful for General Chemistry problems, things do not usually work that way in the real world. In general, a kineticist measures a property of the reactant or product that changes with concentration. Unfortunately, most of the time this measurement depends on the product as well. Your measurements today fit into this category. Luckily, it is easy to correct for the contribution of both reactant and product to the measurement.

Assume a reaction that is first order (or pseudo-first order) of the form



with rate constant k . We measure a property, say the index of refraction of the solution of A and B, N . The contribution of a to the measured index of refraction is $N_A = n_A [A]$ and the total measurement n is given by $N = N_A + N_B = n_A[A] + n_B[B]$. As a function of time, the contribution of A to the measured property decreases in a first order manner while that of B increases according to first order kinetics. In other words,

$$N = n_A[A]_{t=0} e^{-kt} + (1 - e^{-kt})n_B[A]_{t=0}, \quad (A2)$$

where $n_A[A]_{t=0}$ is defined as N at time=0 and $n_B[A]_{t=0}$ is defined as N at time= , assuming that all of the A reacts to form B. Rearrangement of equation A2 yields

$$N = N_{t=0} e^{-kt} + N_{t=} (1 - e^{-kt}) \text{ or rearranging} \quad (A3)$$

$$(N - N_{t=}) = (N_{t=0} - N_{t=}) e^{-kt}, \quad (A4)$$

which looks our normal first order expression. Since we have already shown that the deflection of the laser is directly proportional to the index of refraction, we may substitute the deflection for N in all of equations A1-A4. Now a plot of the natural log of the left side of equation A4 vs. time should yield $-k$. Our only problem now is that we need the value of the deflection at the end of a very slow reaction. Rather than have the student wait for two hours while the reaction goes to completion, we have run the

reactions, noted the deflection at $t =$ for each of the reaction conditions. Although the index of refraction is dependent upon temperature, within experimental error all of the $t =$ values are identical and equal to 3.8 cm. You may simply use this value in your determination of the rate constants.