

EXPERIMENT 4-4

KINETICS OF THE ACID-CATALYZED CONVERSION OF GLYCIDOL TO GLYCEROL

This experiment demonstrates how laser-based measurements of the refractive index of a reaction mixture can yield kinetic information about a chemical reaction, specifically, the acid-catalyzed conversion of glycidol to glycerol.

DEGREE OF DIFFICULTY

Experimental: moderate
Conceptual: moderate to difficult

MATERIALS

- red laser
- test tube (20-mm inner diameter, 50-mL volume)
- 6.0 mL of glycidol (Sigma product #G0887. Approx. \$21 for 100 mL. $d = 1.12$ g/mL. MW = 74.08 g/mol)
- 10 mL of concentrated perchloric acid (~ 60% HClO₄ by weight)
- rubber stopper with one hole for a thermometer
- thermometer
- disposable pipette
- ring stand and clamps
- water bath and ice chips
- magnetic stirrer and stir bar

PROCEDURE

1. In a fume hood, add 6.0 mL of glycidol, 14.0 mL of deionized water, and a stir bar to the test tube. Cap the test tube with a rubber stopper through which a thermometer is inserted.
2. Clamp the test tube over a magnetic stirrer located approximately 2 m from a screen (Figure 4-4-1). Direct the laser so that the beam travels across the diameter of the test tube, and then slowly move the test tube perpendicularly to the laser beam until the angle θ (Figure 4-4-2) reaches a maximum value, at which point the reflected image becomes noticeably sharper. Fix the test tube in this position.

Study of Reaction Kinetics

3. Using a disposable pipette, add 2 drops of perchloric acid to the test tube to initiate the reaction. Monitor the beam displacement as a function of time.
4. Repeat steps 1–3, but use different amounts of perchloric acid. We performed trials with 4, 6, 8, and 10 drops of acid. For 8–10 drops of acid, the reaction is rapid at room temperature and evolves a significant amount of heat; thus, it necessitates the use of a water bath and ice chips to regulate the temperature.

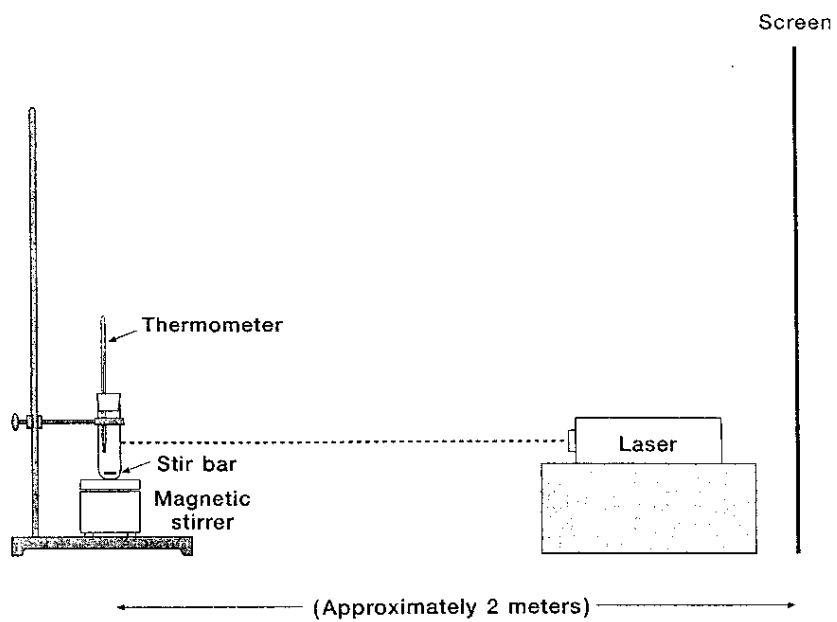


FIGURE 4-4-1. Schematic diagram of experimental setup for monitoring the refractive index of a reaction mixture to obtain kinetic data.

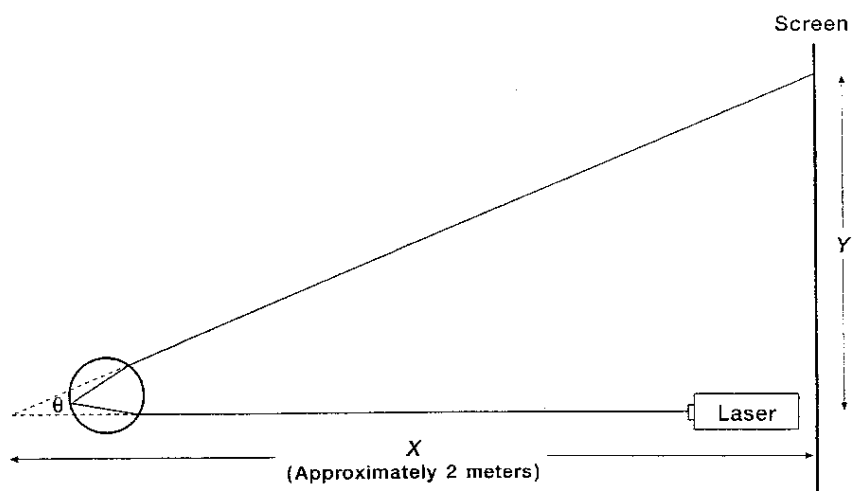


FIGURE 4-4-2. Definition of the distances X and Y and the angle θ .

Determination of Activation Energy (Optional)

5. Repeat the experiment at different temperatures using a constant concentration of perchloric acid and glycidol. Employ a water bath to maintain as constant a temperature as possible. Regulation of temperature is somewhat tricky because of the exothermicity of the reaction but can be accomplished in the well-stirred solution by judicious addition of ice while monitoring the temperature constantly. **Do not lean over the opening of the test tube!** See also a comment on temperature control in the discussion section under "Possible Modifications of Procedure."

HAZARDS AND PRECAUTIONS

Glycidol, as an organic epoxide, is a suspected chemical carcinogen. Glycidol and perchloric acid are both corrosive. Perchloric acid is a strong oxidizer and can cause chemical burns. Glycidol is combustible and requires refrigeration. The reaction can be safely monitored in a large test tube not more than 33% filled with up to 30% (volume) of glycidol in water, beyond which concentration heating effects become significant. Do not perform experiments at higher concentrations! A reaction that we attempted with 60% (volume) glycidol produced dangerous splattering.

DISPOSAL

Neutralize the reaction mixture and dispose of it as organic waste.

DISCUSSION

Glycidol belongs to a class of compounds known as epoxides. Epoxides have in common a three-membered ring that consists of two carbon atoms and one oxygen atom. Compounds containing three-membered rings are rarely highly stable, because the geometry of the ring forces the bond angles between the atoms to be near 60° , much smaller than the 109.5° bond angles normally associated with carbon atoms in sp^3 hybridization states. The decreased stability caused by undesirable bond angles is frequently referred to as *ring strain*.

The ring strain associated with epoxides causes them to be highly reactive, and epoxides generally react in ways that open up the three-membered ring (2). In this experiment, glycidol reacts with water under acid catalysis to form glycerol (Figure 4-4-3). The index of refraction of the product is greater than that of the reactant, and as the reaction progresses, the index of refraction of the reaction mixture increases. A laser

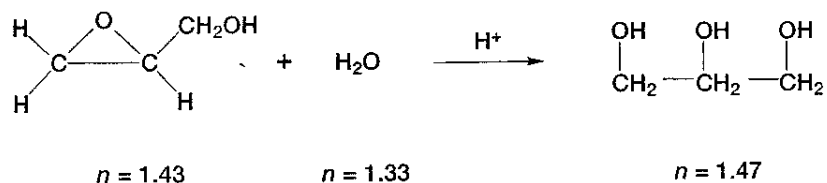


FIGURE 4-4-3. Acid-catalyzed ring opening of glycidol with water.

is used to monitor the index of refraction of the reaction mixture over time, thereby permitting quantitative measurements to be made of rate constants.

How Refractive Index Changes Reflect the Extent of a Reaction

In general, the index of refraction of a mixture (n) is a weighted average of the indices of refraction of the components (n_1, n_2 , etc.)

$$n = n_1X_1 + n_2X_2 + n_3X_3 + \dots \quad (4-4-1)$$

where X_1, X_2 , etc. are the mole fractions of the various components. The reaction studied in this experiment is a three-component system consisting of glycidol, water, and glycerol. For the sake of concreteness, we can name glycidol as compound 1, water as compound 2, and glycerol as compound 3. Because

$$X_1 + X_2 + X_3 = 1 \quad (4-4-2)$$

equation 4-4-1 can be rewritten as

$$n = n_1(1 - X_2 - X_3) + n_2X_2 + n_3X_3 \quad (4-4-3)$$

which can be rearranged to

$$n = n_1 + (n_2 - n_1)X_2 + (n_3 - n_1)X_3 \quad (4-4-4)$$

Filling in numerical values for the indices of refraction gives

$$n = 1.43 - 0.1(X_2) + 0.04(X_3) \quad (4-4-5)$$

Under the reaction conditions employed in this experiment, the value of X_2 remains approximately constant during the course of a reaction, and the first two terms in equation 4-4-5 can be considered constant. The value of X_3 is a measure of the extent of the reaction and ranges from 0 at the outset of the reaction to approximately 0.12 if the reaction goes to completion. Thus, n would be expected to increase linearly with the extent of the reaction. For a more rigorous discussion of the linearity of the refractive index of the mixture versus the extent of the reaction, please see Appendix 4-4-A1 (after this experiment).

Laser-Based Monitoring of the Refractive Index of the Reaction Mixture

The system used to monitor the refractive index is based on an experiment described by Noll (3) that uses a laser to determine the index of refraction of a liquid in a test tube. The usefulness of this technique is that the displacement of the reflected laser beam (Y in Figure 4-4-2) is directly proportional to the refractive index of the solution. The mathematical argument presented by Noll to confirm this fact is somewhat complicated and is summarized in Appendix 4-4-A2. Understanding this argument, however, is not necessary to understand the results of this experiment. Figure 4-4-4 provides an empirical demonstration that the displacement Y is directly proportional to the refractive index by presenting a plot of experimental values of the beam displacement for various solutions of glycerol in water that have indices of refraction that range from 1.33 to 1.39.

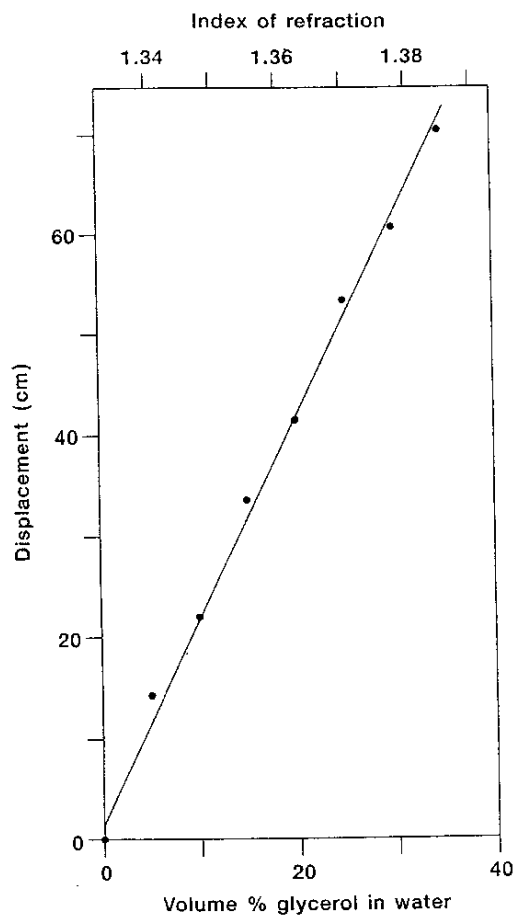


FIGURE 4-4-4. Empirical demonstration that beam displacement is directly proportional to refractive index using solutions of glycerol in water. The beam displacement is referenced to the displacement for pure water.

Experimental Results and the Reaction Mechanism

Figure 4-4-5 depicts the natural logarithm of the displacement (Y) versus time for different amounts of perchloric acid. The logarithm of Y over time is linear for each of the trials, indicating that the reaction is first order with respect to glycidol. This conclusion has been confirmed by two other studies of this reaction (4,5) using a different technique. The rate constants (k) are given by the slopes of the lines.

The accepted mechanism for the conversion of glycidol to glycerol¹ (2) (Figure 4-4-6) helps explain these results. The rate-limiting step in this mechanism is the second

1. Note that addition of water to the molecule occurs at the more highly substituted carbon. This fact has been ascertained by isotopic studies of the reaction (2,5) and initially caused confusion over whether the addition of water followed a concerted reaction or involved two steps—the ring opening of glycidol followed by the addition of water to the resulting carbocation. The current explanation (2) is that the addition of water is *primarily* a carbocation reaction, although the addition occurs by an S_N2 mechanism. The addition occurs at the more highly substituted carbon because the positive charge is more stable there.

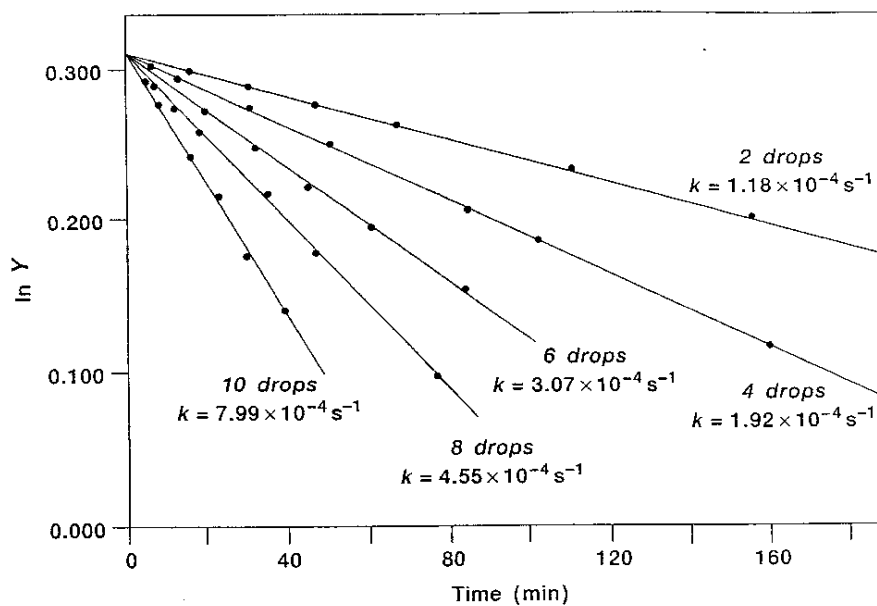
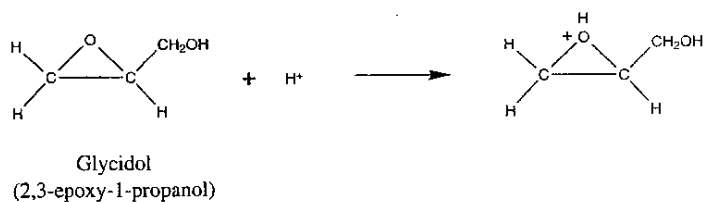


FIGURE 4-4-5. Kinetic data for the acid-catalyzed glycidol-glycerol reaction for various concentrations of perchloric acid.

Step 1: protonation of glycidol



Step 2: nucleophilic attack of water on protonated glycidol

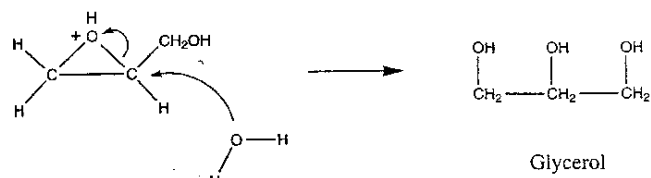


FIGURE 4-4-6. Accepted mechanism for the acid-catalyzed conversion of glycidol to glycerol.

step, the ring opening of protonated glycidol. This step involves two chemical species, and its rate is given by

$$\text{rate} = k_2[\text{water}][\text{protonated glycidol}] \quad (4-4-6)$$

where k_2 is a rate constant. If the rate of the first step is assumed to be so much faster than that of the second step that the first step can be considered to be at equilibrium, then the concentration of protonated glycidol should depend on both the concentration of glycidol and the acid concentration. This fact can be demonstrated by writing the equilibrium expression for the first step as

$$K = \frac{[\text{protonated glycidol}]}{[\text{H}^+][\text{glycidol}]} \quad (4-4-7)$$

(K is the equilibrium constant) and substituting this expression into equation 4-4-6:

$$\text{rate} = k_2 K [\text{water}] [\text{H}^+] [\text{glycidol}] \quad (4-4-8)$$

Because the concentration of water is very nearly constant, equation 4-4-8 can be simplified to

$$\text{rate} = C [\text{H}^+] [\text{glycidol}] \quad (4-4-9)$$

where $C = k_2 K [\text{water}]$. Because the acid is a catalyst, the concentration of H^+ also does not change significantly during the course of the reaction. Thus, to a good approximation, the reaction appears to be a first-order reaction (Figure 4-4-5). Because the reaction is not rigorously first order, however, the rate constants are properly called pseudo-first-order rate constants.

This mechanism also predicts that the pseudo-first-order rate constants should increase linearly with acid concentration. Figure 4-4-7 shows that at lower acid concentrations, the rate constants increase approximately linearly with acid concentration, but that significant deviations from linear behavior are observed at higher acid concentrations. The fundamental explanation for this behavior is that the activity rather than the concentration of the hydrogen ion determines the rate of reaction. In the discussion of the mechanism of the reaction above, we employed the usual assumption that the activity of the various species could be closely approximated by the concentrations of the species. As the ionic strength (electrolyte concentration) of the reaction mixture increases, however, this approximation becomes less valid. Appendix 4-4-A3 provides a more detailed discussion of the dependence of the rate constants on acid concentration.

Determination of the Activation Energy

The activation energy of the reaction can be determined by measuring the rate constant of the reaction at different temperatures. The Arrhenius law states that the rate constant $k(\text{s}^{-1})$ of a reaction changes with temperature $T(^{\circ}\text{K})$ according to the equation

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (4-4-10)$$

where A is a frequency factor (s^{-1}), E_a is the activation energy (J mol^{-1}), and R is the

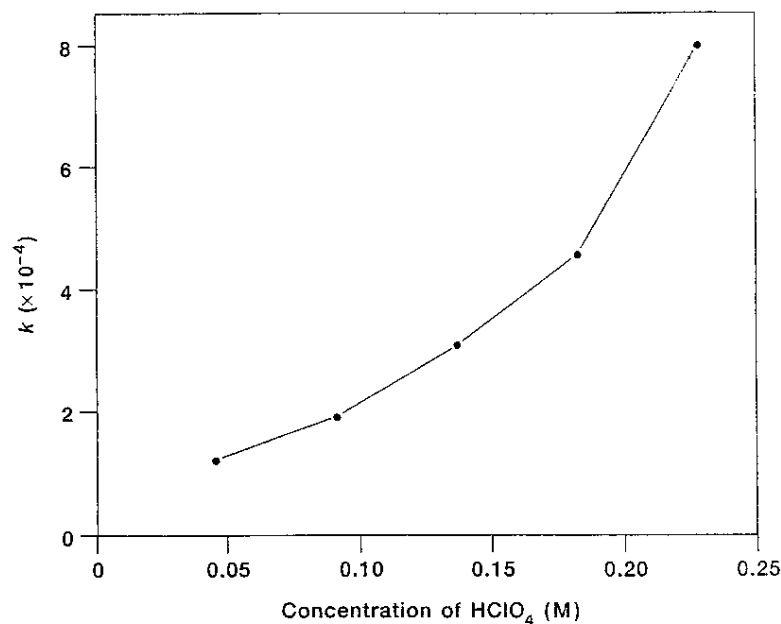


FIGURE 4-4-7. Dependence of pseudo-first-order rate constant (k) on perchloric acid concentration.

gas constant, $8.314 \text{ J } ^\circ\text{K}^{-1} \text{ mol}^{-1}$. Taking the natural logarithm of both sides gives

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4-4-11)$$

Thus, a plot of $\ln k$ vs. $1/T$ allows the determination of the activation energy from the slope of the regression line. Figure 4-4-8a shows the displacement vs. time for the reaction catalyzed by 0.137-M (6 drops) perchloric acid at three different temperatures, and Figure 4-4-8b shows the Arrhenius plot of the rate constants, from which an activation energy of 71.1 kJ/mol or 17.0 kcal/mol was determined.

Possible Modifications of Procedure

Some modifications to this experiment have been noted by those in other teaching laboratories. In particular, Professor Joseph J. BelBruno, Department of Chemistry, Dartmouth College (personal communication) recommends the following modifications:

1. The experiment is performed cooperatively, and each laboratory group is responsible for one of the four sets of conditions from the following table:

Glycidol Concentration (%)	15 μ L of (HClO ₄), M	T, $^\circ$ C
30	6	30
30	6	40
30	6	50
30	3	50