# Laser based measurement of refractive index changes: Kinetics of 2,3-epoxy-1-propanol hydrolysis

**ARTICLE** *in* JOURNAL OF CHEMICAL EDUCATION · SEPTEMBER 1988

Impact Factor: 1.11 · DOI: 10.1021/ed065p835



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# Laser-Based Measurement of Refractive Index Changes

## Kinetics of 2,3-Epoxy-1-propanol Hydrolysis

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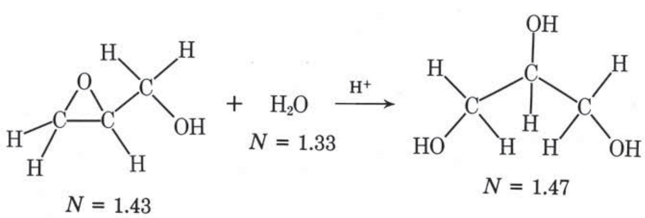
Evidence for chemical change, students are often told, may involve one or more of the following: a color change, a temperature change, gas evolution, precipitation, or other phase changes. However, many chemical reactions appear "invisible" and require some more sophisticated means for detection, usually involving some form of spectroscopy. We describe here a simple laser-based apparatus for measuring the change in the refractive index $n$ during a chemical reaction. We illustrate its use by applying it to follow the kinetics of the acid-catalyzed hydrolysis of 2,3-epoxy-1-propanol, more commonly referred to as glycidol, into glycerol:




When a beam of light passes from air into a homogeneous medium of refractive index $n$, the light beam is bent (refracted) so that the angle of incidence $i$ is related to the angle of refraction $r$ by

$$n = \sin i / \sin r \tag{1}$$

Equation 1 is simply Snell's law where the refractive index of air has been approximated as unity. The refractive index of a liquid can be determined using eq 1 by placing the liquid inside a hollow glass prism and measuring $i$ and $r$. However, such a procedure is experimentally more awkward than using a cylinder (test tube). The latter procedure, introduced by Noll[1], is mathematically more complicated but is much simpler in practice.

Figure 1 shows the experimental setup. Liquid is placed inside a glass test tube (20 mm i.d., 50 mL volume) located about 2 m from a screen. The tube is positioned in front of a He–Ne laser so that the incident beam first approaches along the diameter (point F in Fig. 1). Then the tube is displaced perpendicular to the beam. The beam displacement angle $\theta$ increases then decreases. When $\theta$ is at its maximum value, a sharp image appears on the screen. For these conditions, the angle of refraction $r$, the beam displacement angle $\theta$, and the refractive index $n$ satisfy the relations[1]:

$$\theta = 4r - 2i \tag{2}$$

$$\frac{d\theta}{dr} = 0 \tag{3}$$

$$n^2 = \frac{4}{1 + 3\sin^2 r} \tag{4}$$

1. Noll, E. D. *Phys. Teach.* **1973,** *11,* 307–309.

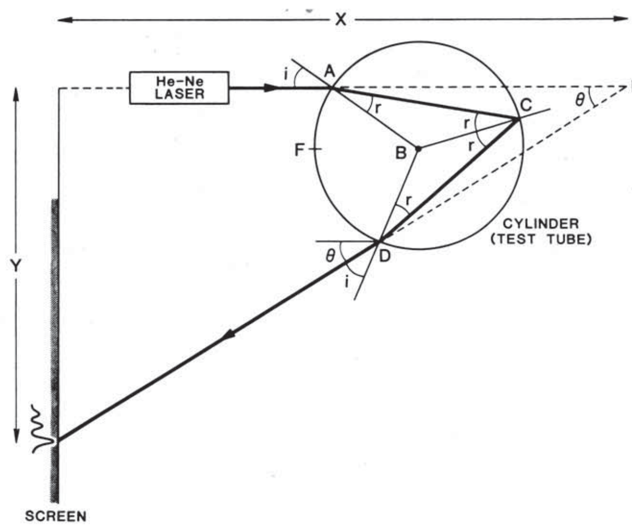



Figure 1. Schematic drawing of the experimental setup showing the angle of incidence $i$, the angle of refraction $r$, and the displacement angle $\theta$. The displacement $Y$ of the image on the screen is related to the displacement angle $\theta$ by $\tan\theta = Y/X$.

and

$$r = \sin^{-1}[(4 - n^2)/3n^2]^{1/2} \tag{5}$$

As the index of refraction changes, so does the displacement $Y$ of the laser beam image on the screen. Indeed, it may be shown to high approximation that $Y$ is linearly related to $n$. (See Appendex.) Hence, by monitoring the displacement of the image on the screen we are able to quantify the change in the index of refraction and thus measure the rate of a chemical reaction whose reactants and products appear not to change by eye but have different values of the index of refraction.

### Experimental Procedure

**Glycidol** (bp 160–161 °C) **is a toxic irritant** and human contact with it or its vapor is to be avoided. The test tube is filled with 6.0 mL glycidol (Aldrich Co.) and 14.0 mL of water in a fume hood, capped with a rubber stopper holding a thermometer, and placed in the monitoring configuration shown in Figure 1. Using a disposable glass pipet, variable amounts of perchloric acid (10.7 M) are added to the reaction mixture, and the screen displacement is monitored as a function of time. For 8 to 10 drops of acid the reaction is very fast at 26 °C and chips of ice need to be added to a water bath to regulate the temperature; for fewer drops of acid, no water bath is needed. It was found that this colorless reaction could be monitored safely by its index of refraction change up to 30% (volume) in glycidol beyond which point the heating effects become significant. An attempted reaction with 60% (volume) in glycidol produced dangerous spatter-

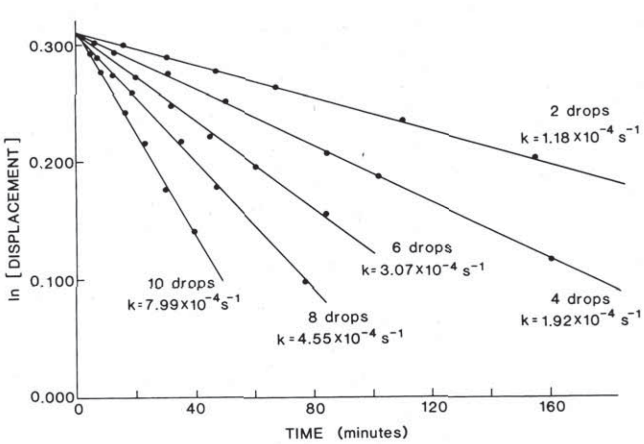



Figure 2. The logarithm of the image displacement vs. time for various numbers of drops added of perchloric acid.

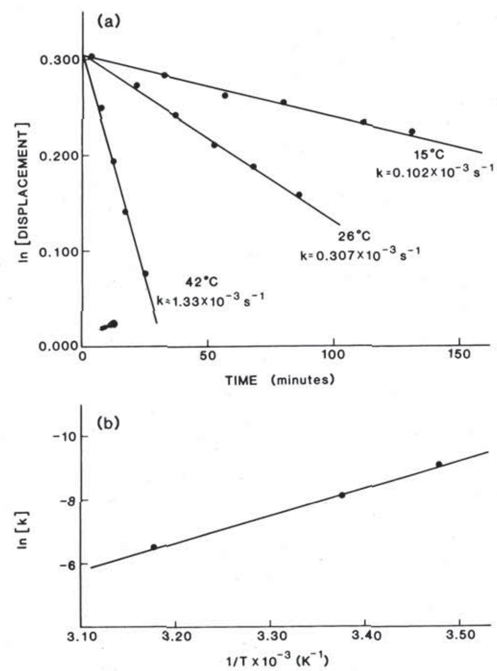



Figure 3. Kinetic data for the acid-catalyzed glycidol–glycerol hydrolysis reaction: (a) logarithm of the image displacement vs. time for reaction mixtures at various temperatures, and (b) the logarithm of the resultant rate constant vs. the reciprocal of the temperature.

ing. Figure 2 shows plots of the natural logarithm of the displacement vs. time.

## Kinetic Analysis

The glycidol hydrolysis has been studied previously by Brönsted, Kilpatrick, and Kilpatrick[2] and by Pritchard and Long[3] using dilatometry. It was established that the hydrolysis is first order in the glycidol concentration. This implies that screen displacement should be proportional to the glycidol concentration and explains why the individual runs in Figure 2 show straight-line behavior. The (pseudo)-first-order rate constants are marked on each run and are found to be roughly linear as a function of $[HClO_4]$ except at the highest value.

The reaction catalyzed by 0.137 M $HClO_4$ was also studied at 15 °C in a water bath by cooling with ice chips and at 42 °C with artful regulation using hot water and ice chips. Figure 3a shows the log of displacement vs. time and Figure 3b plots the resulting first-order rate constants against the reciprocal of temperature. We find an activation energy of 17.0 Kcal/mol for this hydrolysis reaction.

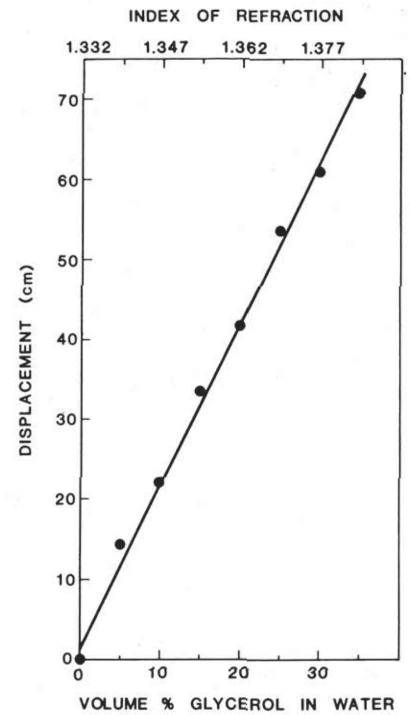



Figure 4. Plot of the displacement of the image on the screen as a function of glycerol volume percent in water, which is proportional to molarity. The linear behavior demonstrates that the displacement is proportional to the value of the refractive index of the liquid in the test tube. The displacement is referenced to the displacement for pure water.

To conclude, the glycidol–glycerol system is one that illustrates a chemical change in a visually unchanged system through laser-based measurement of the refractive index as a function of time. This experiment can be easily adapted for a lecture demonstration before a large group of people. The experiment requires the use of a He–Ne laser and common laboratory materials. The glycidol–glycerol system meets the requirements that (1) there is a significant change in refractive index from reactants to products, (2) both are colorless, (3) the changes in temperature caused by reaction do not overwhelm the index of refraction measurement, and (4) the reaction proceeds at a convenient rate for the refractive index change to be followed visually. Other systems were tried, but none were found to give better performance.

## Appendix

The displacement $Y$ on the screen is proportional to $\tan\theta$ when the change in $X$ is negligible (see Fig. 1). Under our experimental conditions $X$ changes less than 5% of its value during a run. Using eqs 2 and 5 we write

$$Y \propto \tan[4 \sin^{-1}[(4 - n^2)/3n^2]^{1/2} - 2i] \tag{6}$$

This complex relation appears quite forbidding, but numerical analysis shows that for reasonable values of $n$ ($1.33 \le n \le 1.40$) and $i$ ($60° \le i \le 70°$), $Y$ varies linearly with $n$. As an experimental check, various solutions of glycerol in water were prepared and the screen displacement measured for a fixed value of $i$. Figure 4 shows the resulting plot which confirms the validity of the relation $Y/n$ = constant over the range of interest for the study of the acid-catalyzed hydrolysis of glycidol.


## Acknowledgment

This work is supported by the National Science Foundation under NSF MDR 84-70336.



2. Brönsted, J. N.; Kilpatrick, M.; Kilpatrick, M. *J. Am. Chem. Soc.* **1929,** *51*, 428–461.

3. Pritchard, J.G.; Long, F.A. *J. Am. Chem. Soc.* **1956,** *78*, 2667–2670.