

Studying Fast Reactions: Construction and Use of a Low-Cost Continuous-Flow Instrument

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Patrick J. Bisson and James E. Whitten*

Department of Chemistry and Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA 01854;

*James_Whitten@uml.edu

Chemical kinetics is a key topic studied in the physical chemistry curriculum. In standard kinetics experiments reagents are mixed, and measurements are taken to deduce the concentrations of one or more of the reactants or products as a function of time. Such "time-domain" laboratory experiments are adequate when the rate of the reaction is slow enough that several data points may be collected before the reaction has substantially progressed. While methods to study fast reactions are discussed in physical chemistry textbooks (1, 2) and lectures, only a few related laboratory experiments (3–6) appropriate for the undergraduate laboratory have been developed.

The "continuous-flow method" for studying fast reactions consists of mixing two or more reagents in a reaction tube and monitoring the progress of the reaction at different positions along the length of the tube using a traveling photometer. A constant reactant concentration at a particular position along the length of the tube is established as the reagents mix, react, and flow through the tube at a constant velocity (7, 8). This allows the time progression of the reaction to be transformed to space and permits fast reactions to be studied, since a small interval in time can be stretched out over an arbitrarily large distance by increasing the flow velocity in the tube. As an example, if the reaction takes place in only one second, and the flow rate is adjusted so that the reagents transit the length of the tube in one second, then the entire reaction may be studied from beginning to end with very fine time resolution. Since the reactant and product concentration at each location along the tube stays constant, the time required to acquire a measurement does not matter, only position.

The subject of this article is the construction and use of a low-cost continuous-flow apparatus appropriate for the student laboratory. This laboratory augments experiments designed to modernize the physical chemistry laboratory curriculum (9). The absorbance photometer has been constructed from a light-emitting diode (LED) light source and a "photodiode-on-a-chip" integrated-circuit (IC) detector and has a total cost of less than \$20, excluding its power supply. Other components include a quartz reaction tube, two inexpensive chemical transfer pumps, and an aluminum track on which the photometer travels. A novel feature of the instrument is a position sensor consisting of a high resistance iron–nickel alloy wire across which a dc voltage is applied. The traveling photometer makes electrical contact with the wire as it moves along the length of the quartz tube, and the volt-

age it encounters is proportional to position. A two-channel computer interface, such as the LabPro instrument sold by Vernier Software, may be used to monitor simultaneously absorbance and position. The aluminum track and photometer mounting hardware were custom-designed for this project, and detailed machine drawings that can be directly submitted to a machine shop are included in the Supplemental Material.^W The entire cost, including machine shop time, chemical transfer pumps, computer interface, and power supply, is estimated to be less than \$2500.

The reaction of aqueous crystal violet, commonly sold as a chloride salt, with sodium hypochlorite (the active component of household bleach) has been used to test the instrument. Aqueous crystal violet has an absorbance peak at 590 nm, which matches the emission of a commonly available LED. A selection of LEDs emitting a variety of wavelengths is available and may be substituted to permit other reactions to be studied. Of course, it is necessary that either the reactants or products absorb light. In the case of crystal violet and a large excess of sodium hypochlorite, the reaction is complete in less than two seconds and dramatically illustrates this method for studying fast reactions.

Experimental Setup

Figure 1 shows a schematic of the instrument. The track consists of a 4-foot long, 0.5-inch thick piece of aluminum. Not shown are two reservoirs containing reagents whose reaction is to be studied and two low-cost variable-rate chemical pumps (Fisher Scientific 15-077-67) used to transfer the reactants to the mixing tube. A plastic Y-shaped connector combines the reagents and allows them to flow together to the 5-mm i.d., 7-mm o.d. quartz reaction tube (Friedrich & Dimmock 246070100); tygon tubing carries the reagents and joins the Y-connector and quartz tube.

The traveling photometer consists of two components: a 595-nm LED and a photodiode-on-a-chip detector (Burr-Brown OPT101). The latter simplifies construction and contains all the necessary elements (including amplifier) of a photometric detector. The LED and detector are each mounted on separate perforated circuit boards attached to aluminum brackets. The only other electronic component needed is a trim-type potentiometer used to adjust the electrical current and intensity of the LED. As shown, the mounting brackets containing the LED and detector face each other, and a separate 25-mm thick aluminum block with a 5-mm

diameter hole is used as a collimator. This block contains a small hole (5-mm diameter), into one side of which is inserted the LED. A Teflon “V-block”, inserted between the quartz tube and cover of the traveling photometer, stabilizes the tube.

The position of the photometer with respect to the mixer is measured using a high resistance iron–nickel (alloy 875) wire running parallel to the reaction tube. A voltage difference (~ 4 V dc) is applied to the two ends of the wire, and a sliding contact on the photometer picks up the voltage, which is an analog of position. Power for the photometer and LED, and the photodiode and position sensor output signals, are carried to and from the moving photometer via a cable connected to a “break-out-box” that allows convenient connections. A triple output power supply (Instek GPS-3303D) provides all of the power for the experiment. One variable voltage channel of the power supply is set for +30 V dc and

connected to the photometer power terminals (i.e., photodiode power supply) of the break-out-box. The fixed +5 V dc output of the power supply is connected to the LED power terminals, and the second variable output is set to ~ 4 V and connected via alligator clips to the ends of the position sensing wire. The LabPro interface is also connected to the instrument through the break-out-box to measure output voltages from the photodiode IC and the position sensor.

Hazards

Sodium hypochlorite is a strong oxidizer and can be dangerous in high concentration. Crystal violet can stain clothes and skin and may be carcinogenic. It is recommended that gloves be worn when handling concentrated solutions of both reagents. The waste generated from this experiment should be disposed of properly

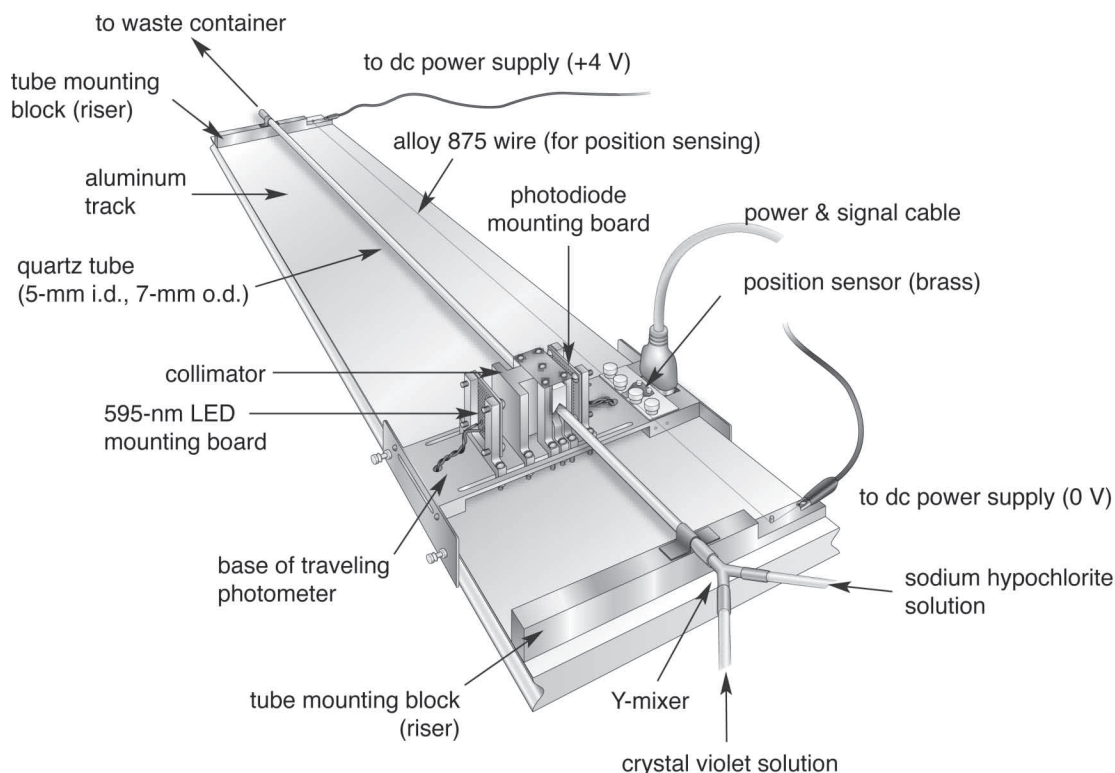


Figure 1. Schematic of the homemade continuous-flow instrument showing the traveling photometer on its sliding optical bench, the position sensor wire, and 1-m quartz reaction tube. The reagent reservoirs, transfer pumps, triple output power supply, break-out-box, LabPro interface, and desktop computer are not shown. Also not shown is a small glass capillary tube transversally inserted into the Y-mixer to increase turbulence and enhance mixing. The tube mounting blocks (risers) are electrically insulated from the aluminum track by the use of nylon washers. More details are provided in the Supplemental Material.¹⁰

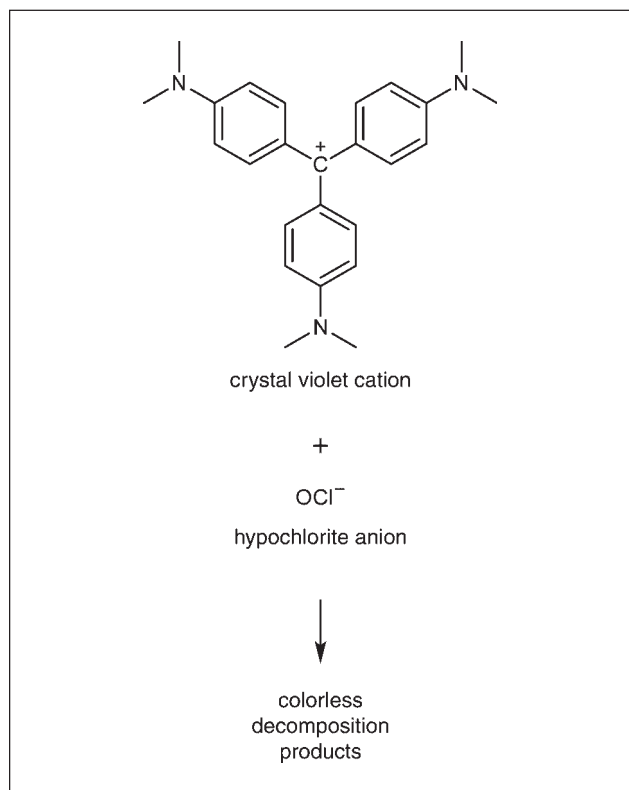


Figure 2. Chemical reaction of aqueous crystal violet cation with the hypochlorite anion. The products are colorless.

Procedure and Results

Figure 2 shows the chemical equation for the reaction of crystal violet with hypochlorite. The reaction involves the formation of one or more colorless products owing to loss of the quinoidal structure of the dye. The details of the decomposition products have not been studied, but the reaction is first order with respect to crystal violet in the presence of an excess of hypochlorite.

A 2-L solution of 81 μM crystal violet (CV) is prepared by dissolving solid CV (Aldrich) in deionized water. Aqueous sodium hypochlorite (2 L, 74 mM) is prepared by diluting a 4–6% stock solution (Fisher Scientific), with the actual concentration determined by absorbance spectroscopy using the known 290-nm extinction coefficient of $350 \text{ cm}^{-1} \text{ M}^{-1}$ (10, 11). The reaction due to mixing equal volumes of 81 μM CV and 74 mM sodium hypochlorite is complete in just seconds. Using the continuous-flow method, a flow velocity of ca. 50 cm/s is reasonable and corresponds to a transit time of approximately two seconds through the 1-m reaction tube. The inside diameter of this tube is 0.5055-cm, yielding a discharge rate of 0.9 L in 90 s.

After balancing the flow with water, a measurement is accomplished by moving the photometer to the position closest to the mixer. The Logger Pro software is set to record 25 voltage measurements per second in each of the two channels. A "blank" is measured by pumping water through the reaction tube, starting data recording, and moving the photometer steadily from the mixer end to the discharge end in ca. 10 s. This measurement is then repeated, but with the reagents flowing instead of water. For the described reaction

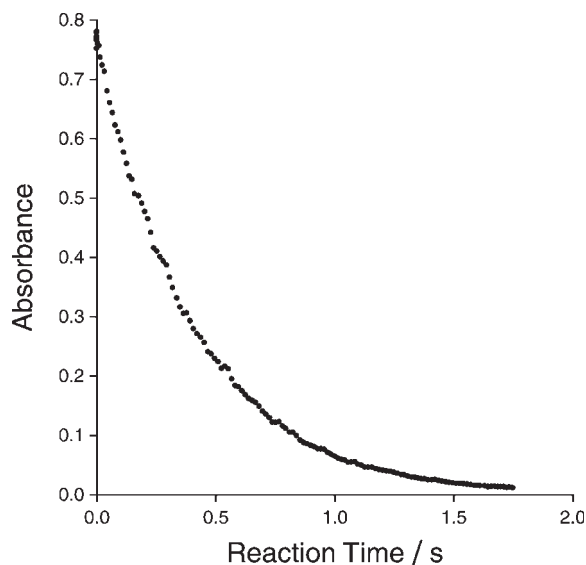


Figure 3. Plot of 595-nm absorbance versus time for an aqueous mixture containing 40.5 μM crystal violet and 37 mM sodium hypochlorite. The reaction time is obtained by transforming position along the reaction tube to time using eq 3. The flow velocity of the reaction mixture is 57.3 cm/s.

conditions, a dramatic color gradient is observed from the mixer end where it is most intense to the outlet end where it is colorless. Three passes (i.e., strokes) of the photometer may be recorded in a total elapsed time of about one minute to measure the precision of the results. With some planning, the entire experiment may be performed with the generation of about 750 mL of waste.

Following acquisition, the data are transferred to an Excel spreadsheet. The "blank" stroke data are averaged over the length of the stroke to produce a single value, R , and absorbance is calculated using

$$\text{Absorbance} = -\log\left(\frac{S}{R}\right) \quad (1)$$

where S is the raw photodiode voltage (as a function of position). The position is calculated as

$$\text{position} = \frac{V_{\text{sense}} - V_{\text{min}}}{V_{\text{max}} - V_{\text{min}}} \times \text{stroke length} \quad (2)$$

where V_{sense} is the raw output voltage from the position sensor and V_{max} and V_{min} are the voltages at the end and beginning of the stroke, respectively. Position is transformed to reaction time using the flow velocity:

$$\text{reaction time} = \frac{\text{position}}{\text{flow velocity}} \quad (3)$$

Figures 3 and 4 show typical graphs, obtained by an undergraduate physical chemistry student, of absorbance and the natural log of absorbance versus reaction time, respec-

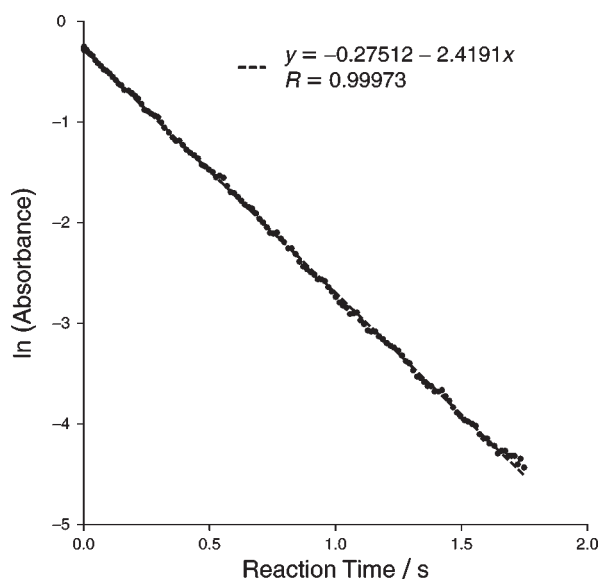


Figure 4. Plot of natural log of absorbance vs time for the data shown in Figure 3. The equation given in the graph is from a linear regression of the data. The linearity of the plot indicates first-order kinetics with respect to crystal violet, with a pseudo-first-order rate constant, 2.4 s^{-1} . The temperature of the reagents prior to mixing was 23°C .

tively. In the latter case, the linearity of the graph indicates first-order kinetics. Because a large excess of sodium hypochlorite is used, its concentration is essentially constant, and the reaction is first order with respect to CV, with a pseudo-first-order rate constant of 2.4 s^{-1} , given by the negative of the slope of the linear fit through the data. The experiment may be repeated using a different concentration of sodium hypochlorite (e.g., 25 mM after mixing in the tube) to show the kinetics are also first order in this reactant. Once established, the true rate constant may be found by dividing the pseudo rate constant by the hypochlorite concentration. We have determined this as $63 \text{ M}^{-1} \text{ s}^{-1}$. To the best of our knowledge, this is the first report of the measurement of this rate constant.

It is important to note that hydroxide competes with hypochlorite for reaction with CV, and this must be considered when selecting different hypochlorite concentrations. For the conditions used, the pH of the reaction mixture is 10.9. Using simple absorbance versus time measurements, we have measured the rate constant of the competing reaction with hydroxide as $0.174 \text{ M}^{-1} \text{ s}^{-1}$. Thompson and Ting (12) have measured the rate constant of this reaction at a variety of temperatures, and the data from their Arrhenius plot yield a value of $0.138 \text{ M}^{-1} \text{ s}^{-1}$ at 23°C , in reasonable agreement with our experimentally determined value. Because the competing reaction of crystal violet with hydroxide is orders of magnitude slower than with hypochlorite, it may be neglected for large hypochlorite concentrations, such as those used in this study.

Conclusions

The construction and use of a low-cost continuous-flow instrument for measuring the kinetics of fast reactions have

been demonstrated. Novel features of its design include the use of an LED light source, a photodiode-on-a-chip detector, and a position sensor. This instrument is suitable for the physical chemistry laboratory and permits reactions that take place in less than a few seconds to be studied. Its performance has been demonstrated for the reaction of CV with sodium hypochlorite. This instrument could, in principle, be used to study the kinetics of various fast reaction that result in a color change. These include reactions of dyes with oxidizing agents and reactions that proceed from a colorless reaction mixture to a colored product (e.g., acid–base reactions with an appropriate indicator). Relatively fast reactions that form the dark red iron(III)–thiocyanato complex (4, 5) would also be candidates for student laboratory studies. A large selection of LEDs are currently available that emit wavelengths ranging from 390 to 660 nm, and the only modification necessary to study another reaction is to select an LED whose emission matches the optical absorbance spectrum of the colored reactant or product.

Supplemental Material

A complete set of drawings that may be submitted to a machine shop, photographs of the apparatus, and a student handout are available in this issue of *JCE Online*. Alternatively, the authors will happily provide either electronic files or printouts of these upon request.

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