#### Gerald Corsaro University of Akron Akron, Ohio

# A Colorimetric Chemical Kinetics Experiment

This article describes an experiment in which a photocolorimetric technique is employed to follow a himolecular reaction rate. The reactants are conic species, one of which is the highly colored dye, crystal violet, and the other, hydroxide ion. The reaction product is colorless so that by measurement of the loss of color intensity of the dye after different time intervals, the bimolecular rate constant can be evaluated directly from the absorbance readings taken with the colorimeter. A Klett-Summerson photocolorimeter with a number 55 filter was used to obtain the data reported in the present article, but a spectrophotometer using a wavelength of 500 ms can be used.

The structure of crystal violet is given as

$$\begin{bmatrix} N(CH_{a})_{b} \\ \vdots \\ N(CH_{a})_{b} \end{bmatrix} = \begin{bmatrix} N(CH_{a})_{b} \\ \vdots \\ N(CH_{a})_{b} \end{bmatrix} \begin{bmatrix} N(CH_{a})_{b} \\ \vdots \\ N(CH_{$$

The contribution of (I) to the resonance hybrid suggests an electron deficiency at the tertiary earbon position, and hydroxide ion may be expected to attack this position to form the colorless carbinol derivative. The reaction is thus essentially one between two oppositely charged monovalent ions and as such should be sensitive to the ionic strength of the reaction medium as predicted by the Bujusted salt effect.

#### The Experiment

A stock dye solution is prepared by dissolving 0.028-0.030 g of the crystal violet dye in one liter of solution. A 0.100 M solution of sodium hydroxide is also required.

A typical rate determination is carried out as follows. Ten ml of dye solution is diluted to 50 ml with water in a 50 ml graduate. Four ml of NsOH solution is diluted in another 50 m graduate to 50 ml with water. The use of graduates rather than volumetric flasks is preferred since the mixing of the solutions to provide the reaction mixture may be done with very little time loss. A stop watch is started simultaneously with mixing the two solutions into a flask. The cuvette used with the instrument is filled with the reaction mixture and stoppered. Absorbance readings (log  $I_0/I$ ) are observed for the reaction mixture at 3-4 min intervals until six to eight readings have been obtained.

A reference graph may be obtained by diluting 2, 4, 6, 8, and 10 ml of dye solution to 100 ml in a volumetrie flask, measuring the absorbance of each solution, and then plotting these values versus ml dye solution used. A linear plot passing through the origin should be obtained. The slope of this plot should be carefully estimated. The slope × 10 will be designated by [A].

The experiment described is repeated using 10 ml dye and 8 ml NaOH. Less than 4 ml of 0.100 M NaOH gives satisfactory results, but it has been observed that the reaction goes to completion only when four or more ml NaOH are used. Variation in initial reactant concentrations is necessary to verify the order of the reaction.

In another series of three experiments the procedure given above is repeated with 8 ml NaOH solution plus 2, 6, and 8 ml 1.0 M KNO, before dilution to 50 ml. This will provide data to test the Brønsted primary salt effect.

The student should be advised that a flooding technique is employed in the experiments. The dye concentration is of the order of  $1 \times 10^{-5} M$  while that of the hydroxide ion is  $4\text{--}8 \times 10^{-5} M$ . Hence, when all of the dye has reacted, the NaOH concentration remains virtually the same as it was initially.

The general form of the rate law is given by

$$\frac{-d[dye]}{dt} = b_{i} \cdot |OH^{-}|^{\alpha} |dye|^{\alpha}$$
(1)

and the flooding condition is indicated by

in which the zero subscript represents initial concentrations. The above conditions give rise to a pseudorate law given by

$$\frac{d[dye]}{dt} = k_{\mu\nu} |OH^{-}|^{\alpha}$$
(3)

in which  $k_{ps}$  is the pseudo rate constant, and

$$k_{ps} = k_1 \cdot [OH^{-}] =$$
 (4)

The problem confronting the student is to determine a and m along with  $k_2$ . The sum, n + m, gives the over-all order of the reaction and the rate constant,  $k_2$ for the reaction.

<sup>&</sup>lt;sup>1</sup> La Mins, V. K., Chem. Rev., 10, 179 (1932).

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