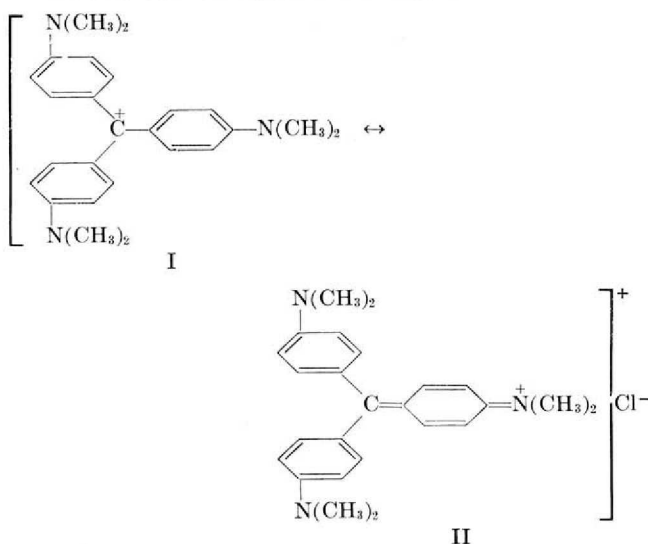


A Colorimetric Chemical Kinetics Experiment

This article describes an experiment in which a photocolorimetric technique is employed to follow a bimolecular reaction rate. The reactants are ionic 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 590 mμ can be used.

The structure of crystal violet is given as



The contribution of (I) to the resonance hybrid suggests an electron deficiency at the tertiary carbon 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 Brønsted salt effect.¹

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 NaOH solution is diluted in another 50 ml 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 volumetric 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 $\times 10$ will be designated by $[A]_0$.

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 KNO₃ 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 1×10^{-5} M while that of the hydroxide ion is $4\text{--}8 \times 10^{-3}$ 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

$$-\frac{d[\text{dye}]}{dt} = k_2 \cdot [\text{OH}^-]^m [\text{dye}]^n \quad (1)$$

and the flooding condition is indicated by

$$[\text{OH}^-]_0 \gg [\text{dye}]_0 \quad (2)$$

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

$$\frac{d[\text{dye}]}{dt} = k_{ps} \cdot [\text{OH}^-]^n \quad (3)$$

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

$$k_{ps} = k_2 \cdot [\text{OH}^-]^m \quad (4)$$

The problem confronting the student is to determine n 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.

¹ LA MER, V. K., *Chem. Rev.*, **10**, 179 (1932).

Integration of equation (3) may be carried out with $n = 1$. In this case one obtains

$$\log \frac{[\text{dye}]_0}{[\text{dye}]_t} = 2.3 k_{ps} t \quad (5)$$

in which $[\text{dye}]_0$ and $[\text{dye}]_t$ are the initial dye concentration and the dye concentration after t min.

If the calibration plot of ml dye versus absorbance is linear, then

$$\frac{[\text{dye}]_0}{[\text{dye}]_t} = \frac{[A]_0}{[A]_t} \quad (6)$$

and substituting (6) into (5) yields

$$\log [A]_t = \log [A]_0 - 2.3 k_{ps} t \quad (7)$$

so that a plot of $\log [A]_t$ versus t should be linear with a slope equal to $-2.3 k_{ps}$. If this plot is not linear, then $n \neq 1$, and $n = 2$ should be tried in (3) and the expression integrated.

After n has been determined the value for m is required. Equation (4) contains two unknowns since k_{ps} may be determined. Two separate experiments in which $[\text{OH}^-]' \neq [\text{OH}^-]''$ are required. From these experiments two k_{ps} values are obtained so that

$$k_{ps}' = k_2 \cdot [\text{OH}^-]'^m \quad (8)$$

$$k_{ps}'' = k_2 \cdot [\text{OH}^-]''^m \quad (9)$$

and k_2 and m may be found by solving (8) and (9) simultaneously.

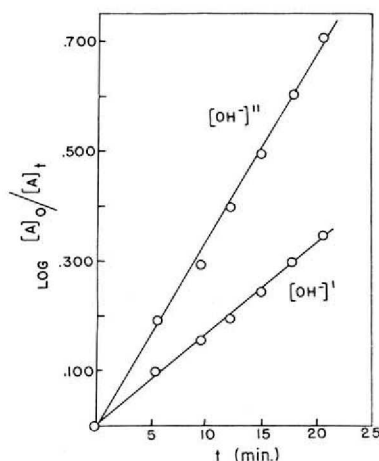


Figure 1. $\log [A]_0/[A]_t$ versus time for $[\text{OH}^-]'' = 2[\text{OH}^-]'$

Figure 1 shows a plot of $\log [A]_0/[A]_t$ versus t for the two sets of OH^- concentrations (10 ml dye + 8 ml NaOH and 10 ml dye + 4 ml NaOH).

The table is a summary of all the rate data obtained in the experiments.

ml NaOH	[KNO ₃]	k_2 (l mole ⁻¹ min ⁻¹)	$g(\mu)^a$
4	0.00	9.57	0.06
8	0.00	9.64	0.09
8	0.02	8.49	0.144
8	0.06	7.35	0.207
8	0.08	6.99	0.228

^a $g(\mu) = (\mu^{1/2})/(1 + \mu^{1/2})$ (see text).

The last three lines of the table show the effect of increasing ionic strength on the reaction rate. The effect noted is the expected one for an ionic reaction

between oppositely charged ions. The Brønsted¹ theory focuses attention on the fact that ionic reactants are thermodynamic entities and as such are subject to the laws of thermodynamics. According to the transition state theory a reaction proceeds through the formation of an activated intermediate. Thus, for the ionic reaction,



the activated complex has a net charge which is the sum of those on the reactant ions. The rate constant for the reaction can be expressed as

$$k_2 = \text{constant} \cdot \frac{f_A f_B}{f_{(\text{AB})}} \quad (10)$$

in which the "constant" is taken as the rate constant for the reaction at zero ionic strength. The terms f_A , f_B represent the ionic activity coefficients of reactants A and B, and $f_{(\text{AB})}$ that for the complex, (AB).

The magnitude of k_2 should thus vary with any environmental condition which alters the activity coefficient ratio, $(f_A f_B)/f_{(\text{AB})}$. Since the reactants are ion species, a variation of reaction mixture ionic strength will affect $(f_A f_B)/f_{(\text{AB})}$ according to the net charge on A, B, and the complex (AB). Since the individual ionic activity coefficients cannot be measured, the Debye-Hückel expression for them may be used.

$$-\log f_i = A z_i^2 g(\mu)$$

where μ is the ionic strength calculated from molal concentrations. In solutions of this dilution these can be taken to be molarities. The Debye-Hückel constant A has the value 0.51 at 25°C. The function $g(\mu)$ is given by the expression:

$$g(\mu) = \frac{\mu^{1/2}}{1 + a B \mu^{1/2}}$$

where a = ion size parameter and is equal to 3 Å for NO_3^- and K^+ .⁵ B = constant = 0.33×10^8 so that the product of the constant terms $aB \sim 1.0$. Hence the expression for $g(\mu)$ simplifies

$$g(\mu) = \frac{\mu^{1/2}}{1 + \mu^{1/2}}$$

This function $g(\mu)$ replaces the $\mu^{1/2}$ term usually given for the Debye-Hückel limiting law so that the theory may apply over a wider ionic strength range.

An expression is obtained

$$\log k_2 = \log k_0 + 2A z_a z_b \cdot g(\mu) \quad (12)$$

which predicts values for $\log k_2$ if $\log k_0$ is known. If the observed values for k_2 are in agreement with theory according to (12) one may take this as evidence for the transition state concept. It must be carefully noted that equation (12) can be obeyed only if the ionic activity coefficients are correctly predicted by the Debye-Hückel equation (11), that no association takes place between reactant ions and their own counter ions or other ions added to alter the ionic strength, or in general that specific ionic effects are absent. Gross deviations from theory have been observed in some cases² but when the effects of association are taken into

² OLSON, A. R., AND SIMONSON, T. R., *J. Chem. Phys.*, **17**, 1167 (1949).

⁵ KIELLAND, J., *J. Am. Chem. Soc.*, **59**, 1675 (1937).

account, the experimental data can be resolved within the framework of theory.^{3, 4}

From the data of the table, equation (12) can be used to test the Brønsted concept. First, one determines the value for $\log k_0$,

$$\log k_0 = \log k_2 - 2Az_a z_b \cdot g(\mu)$$

in which k_2 , the rate constant obtained with 8 ml NaOH and no KNO_3 , is substituted in the equation along with $g(\mu) = 0.09$. Then,

$$\log k_0 = 0.9841 + (1.02)(0.09) = 1.0759$$

Using the values for $g(\mu)$ listed in the table for experiments with KNO_3 , one obtains

$$\log k_2 = 1.0759 - (1.02)(0.144) = 0.929$$

$$\log k_2 = 1.0759 - (1.02)(0.207) = 0.865$$

$$\log k_2 = 1.0759 - (1.02)(0.228) = 0.843$$

The experimentally observed values are 0.940, 0.860, and 0.837, respectively, and are in good agreement with the predicted values. An alternate procedure would be to plot the experimental $\log k_2$ values versus $g(\mu)$ and determine whether or not a linear plot with a slope $= 2Az_a z_b (\sim -1.0$ in this case) is obtained (see Fig. 2).

The whole experiment, including the salt effects, can be done within a three hour laboratory period once the solutions have been prepared. If the entire experiment is not done at one time, each part takes about one hour.

³ DAVIES, C. W., AND WILLIAMS, I. W., *Trans. Faraday Soc.*, 1547 (1958).

⁴ CORSARO, G., AND MORRIS, M., *J. Electrochem. Soc.*, 108, 689 (1961).

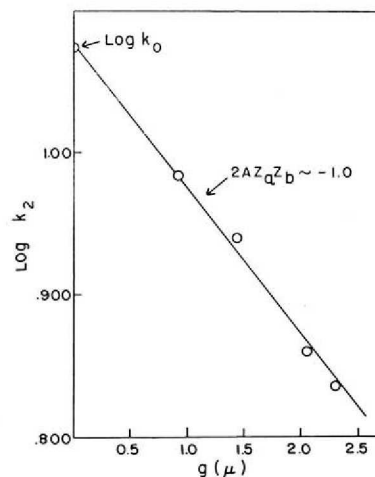


Figure 2. Rate constant, $\log R_2$, versus ionic strength function, $g(\mu)$. The data points are seen to fall on the line predicted by the Debye-Hückel theory with a slope of -1.0 .

The experiment is simple and precise. It may be extended to include effects of temperature and estimation of the energy of activation. Moreover, the salt effect may be studied for a number of salt concentrations less than 0.1 M KNO_3 so that equation (7) can be verified by plotting $\log k_2$ results versus $g(\mu)$. It should be noted that good results for the effects of variation of ionic strength are possible only if all the experiments are done at the same constant temperature. All of the data recorded here was obtained at room temperature.