CRYSTAL VIOLET REACTION

Purpose

The purpose of this experiment is to determine how the rate constant for a reaction changes with ionic strength of the solution and with temperature.

INTRODUCTION: The experiment follows a procedure described in J. Chem. Ed., **41**, 48 (1964). By using the UV-VIS spectrophotometer the rate constant k is measured for the reaction

$$\mathrm{CV^+:Cl^-\left(violet\right)+OH^- \rightarrow CV{:}OH\left(colorless\right)+Cl^-}$$

Here $\mathrm{CV^+:Cl^-}$ is crystal violet, a violet-colored organic dye of molecular weight 408.0, which reacts with OH^- to form a colorless complex. The reaction is studied at three temperatures to determine the activation energy, and at three ionic strengths (at one temperature) to determine the effect of inert electrolytes on the rate constant.

THEORY: We assume the rate law for reaction (1) is

$$\frac{d\left[\mathrm{CV^+}\right]}{dt}=-k\left[\mathrm{CV^+}\right]\left[\mathrm{OH^-}\right]$$

If $\left[\mathrm{OH^-}\right]>>\left[\mathrm{CV^+}\right]$, then $\left[\mathrm{OH^-}\right]$ remains approximately constant during the reaction, and

$$\frac{d\left[\mathrm{CV^+}\right]}{dt}=-k'\left[\mathrm{CV^+}\right]$$

where $k'=k\left[\mathrm{OH^-}\right]$

Integration of (3) between $t=t$ and $t=0$ yields

$$\ln\frac{\left[\mathrm{CV^+}\right]_t}{\left[\mathrm{CV^+}\right]_0}=k't$$

If concentrations are determined by a spectrophotometer we can use the relation

$$\frac{\left[\mathrm{CV}^{+}\right]_t}{\left[\mathrm{CV}^{+}\right]_0}=\frac{A_t}{A_0}$$

where *A* is the absorbance.

Using (5) and (6) we obtain

$$\ln A_t = \ln A_0 - k't$$

Thus k' can be determined from a plot of ln A_t vs. t; because (OH^-) is known, the rate constant *k* can then be calculated from (4).

According to transition-state theory the rate constant at a given temperature for a bimolecular reaction varies with the total ionic strength, μ, of the system,

$$\ln k = \ln k^0 + B\sqrt{\mu}$$

μ can be calculated from the charges, z_i, and the molarities, c_i, of <u>all</u> ions in the system:

$$\mu = \frac{1}{2}\sum_i z_i^2 c_i$$

The value for B can be determined (if the plot of $\ln k$ vs. $\sqrt{\mu}$ is linear) and compared with the theoretical value, thereby testing the validity of the theory for this system. (B is the slope.)

The Arrhenius activation energy, E_A, appears in the equation

$$\ln\frac{k_2}{k_1} = -\frac{E_\mathrm{a}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \text{ or } \ln k = -\frac{E_\mathrm{a}}{R}\left(\frac{1}{T}\right)+\mathrm{Constant}$$

From a plot of $\ln k$ vs. $1/T$ (absolute temperature), at constant ionic strength, E_A can be determined if the plot is linear. The slope is $-E_A/R$.

EQUIPMENT AND CHEMICALS

Visible spectrophotometer (P. E. Lamba 3, Turner 350, Coleman 124)
Crystal violet (0.03 *g/l*),
Electrolyte solutions may be prepared by dissolving a quantity of KNO_3 in 0.008*M* NaOH (For example 0.002 mole KNO_3 dissolved in 50 *ml* 0.008M NaOH.)

PROCEDURE: A stock solution containing 0.030*g* of $CV^+ \cdot Cl^-$ per liter is available. Part A of the experiment requires the determination of *k* at three different ionic strengths but at one temperature, 25°C. For each determination, 50 *ml*. of 0.006*g./l* solution of CV^+Cl^- is mixed briefly with 50 *ml*. of an electrolyte solution; a portion of the mixture is then placed in the sample cell (water is in the other cell), and values for absorbance of solution are recorded every minute for about 15 minutes.The spectrophotometer wavelength is set at the position of highest absorbance (about 586 *nm*) as determined with a non reacting solution of CV^+Cl^-. The first 50 *ml*. portion of electrolyte used is 0.008 *M* in NaOH; the portion used for the second run is 0.008 *M* in NaOH and 0.04 *M* in KNO_3; for the third run the concentrations in the 50*ml*. portion are 0.008 *M* NaOH and 0.16 *M* KNO_3. (Note: You cannot get a solution that is 0.008*M* NaOH and 0.04*M* KNO_3 by mixing 0.008*M* NaOH and 0.04*M* KNO_3. Since the solutions are diluted 1:1 in each other, concentrations are reduced by one-half.)

In part B of the experiment, k is determined at the temperatures 25°C, 30°C, and 35°C, with the 50*ml*. electrolyte portion being 0.008 *M* in NaOH and no KNO_3 present. As before the other 50 *ml*. portion to be mixed contains 0.006*g*. of CV^+Cl^-/l.

CALCULATIONS: For each run calculate A_t and $\ln A_t$ at every time *t*. Plot $\ln A_t$ vs. *t* and determine k'; then calculate *k* from equation 4. For runs in part A calculate and determine B in equation 9. Remember, the 50 *ml*. electrolyte portions were diluted 1:1. From the runs in part B determine E_A in (11). Prepare tables and graphs displaying the above data and results. Discuss the validity of equations 8 and 11 for this system.