THE KINETICS OF FORMALDEHYDE SULFONATION
THE FORMALDEHYDE CLOCK REACTION (#8.4)

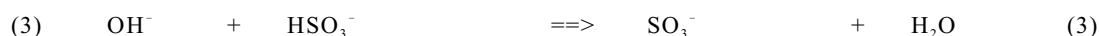By Dale A. Hammond, PhD, Brigham Young University Hawaii

Learning Objectives

The objectives of this experiment are to...

- determine the rate law for the reaction between formaldehyde and bisulfite ion.

- determine the activation energy for the above reaction.

- understand the nature of a "pseudo" kinetic reaction.

Background

Kinetics is the study of "how fast" and "how" a reaction occurs. This experiment will only deal with "how fast," accepting a previously defined three step mechanism. This particular type of experiment is normally a "clock reaction," in which one monitors the time required for a change to occur in the color of the solution, for example, from a light yellow green to deep blue due to the presence of bromothymol blue indicator. However, in this instance we will monitor the time required by a change in the acidity (PH) of the solution. The three step reactions that are believed to cause these changes were discussed by T. Cassen, *Journal of Chemical Education,* 1976, 53, 197. and are as follows:

(1) $\quad HCHO \quad + \quad HSO_3^- \qquad ==> \quad HOCH_2SO_3^- \qquad\qquad$ (1)

(2) $\quad H_2O \quad + \quad HCHO \quad + \quad SO_3^{2-} \quad ==> \quad HOCH_2SO_3^- \quad + \quad OH^- \quad$ (2)

(3) $\quad OH^- \quad + \quad HSO_3^- \qquad\qquad ==> \quad SO_3^- \qquad\qquad + \quad H_2O \qquad$ (3)

A discussion is provided on the supposed reaction mechanism and the cause of the sudden increase in $[OH^-]$ when all of the HSO_3^- is consumed.

Reaction Order and Rate Constant

The rate of reaction between the formaldehyde and the HSO_3^- / SO_3^{2-} buffer can be expressed as

$\qquad$ rate = k $[HCHO]^x [HSO_3^- / SO_3^{2-}]^y$ $\qquad\qquad\qquad\qquad\qquad$ (4)

The constant "k" is a proportionality constant known as the rate constant, and it is constant at a given temperature, but varies with temperature. The values of x and y are termed the "order of the reaction" for each reactant.

Activation energy

Chemical reactions occur as a result of a collision between particles. The amount of energy required for the reaction to proceed is known as the activation energy, Ea. The rates of most reactions increase as temperature increases because the average kinetic energy of the reactants increase and the number of molecules that possess that minimum "activation energy" increases.

The Svante Arrhenius' equation k $= Ae^{-Ea/RT}$ $\qquad$ (5) $\qquad$ is discussed.

Experimental Procedure

The pH probe will be used to monitor the change in pH to determine the reaction time.. Students will then take the first derivative of the pH vs. time curve to determine the precise reaction time.

Mixing the solutions

The proper amounts of solid chemicals are weighed, dissolved in distilled water and mixed well

The Experiments

A series varying concentrations of solution A, containing $NaHSO_3$ and Na_2SO_3, are mixed with a fixed amount of solution B, containing formaldehyde; then varying concentration of B with a fixed amount of A,, to determine the effect of concentration of SO_3^{2-} and formaldehyde on the reaction rate. A third series of reactions with fixed amounts of A and B but at varying temperatures from about 10 ˚C to 50 ˚C to determine the effect of temperature and to determine the activation energy.

Data Analysis

Guidance is given in determining the first derivative in order to determine reaction times, and in calculating the rate law exponents and activation energy.

Instructor Resources Provided

- Sample Report Sheets providing the format to organize the data collection with sample data.

- Questions to consider, answer and turn-in with suggested answers.

- Tips and Traps section to assist the instructor with potential problems and solutions.

- Sample *MicroLAB* screen shots and graphs.

- Laboratory preparation per student station.
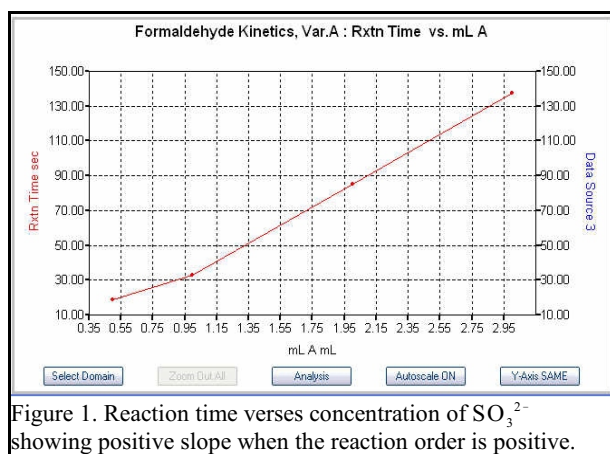
Figure 1. Reaction time verses concentration of SO_3^{2-} showing positive slope when the reaction order is positive.
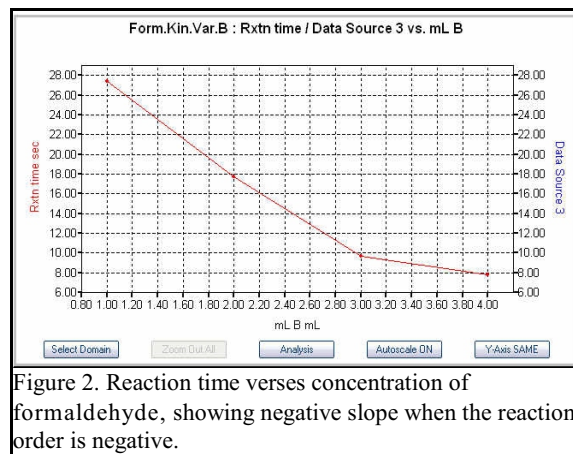

Figure 2. Reaction time verses concentration of formaldehyde, showing negative slope when the reaction order is negative.
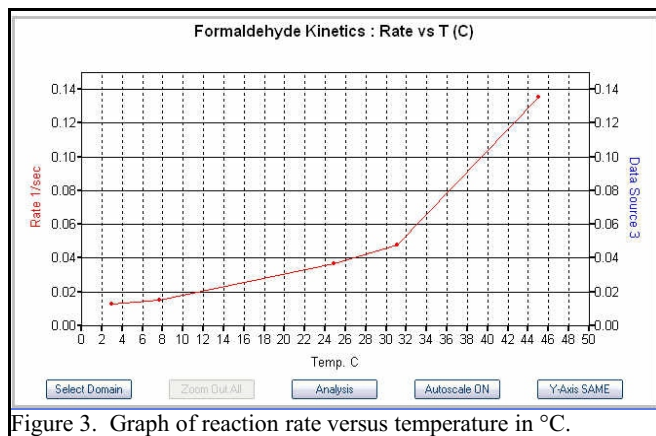

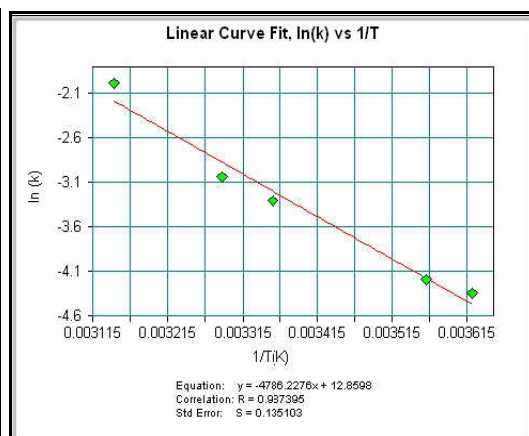
Figure 3. Graph of reaction rate versus temperature in °C.

Figure 4. Graph of ln(K) versus 1/T (K). E_a is calculated as slope (-4786.2 K)*R(8.314 J/K mol)