

CHEM 361 L

EXPERIMENT 8

Kinetic Isotope Effects

(revised January, 2014)

Introduction

Replacing a hydrogen in a molecule with a deuterium has been shown to affect the rates of some reactions. A covalent bond to deuterium should be stronger than the same bond to a hydrogen, due to the reduced mass dependence of the fundamental frequency:

$$\nu = (1/2\pi c)(k/\mu)^{1/2}$$

where ν is the frequency (cm^{-1}), k is the force constant, μ is the reduced mass, and c is the speed of light. A decrease in the fundamental frequency will result in a decrease of the zero-point energy, and this leads to the observed bond strengthening. We would expect reactions for which the breaking of a bond to hydrogen is the rate-determining step to be slower when that hydrogen is replaced by deuterium. This is known as the *Primary Kinetic Isotope Effect*, and the ratio of the rate constants (k_h/k_d) is on the order of 6 to 7.

A *Secondary Kinetic Isotope Effect* may also be observed, due to the fact that D_3O^+ is a stronger acid than H_3O^+ . This will result in a greater degree (by a factor of approximately 3) of basic dissociations in D_2O relative to H_2O . If a reaction involves rapid protonation followed by slower decomposition of the conjugate acid, the reaction will proceed more rapidly in D_2O , due to the higher concentration of deuterated conjugate acid. In this experiment, you will follow the rate of mutarotation of α -D-glucose in both water and D_2O . Both effects are observed in this case. The hydroxyl groups on the sugar are all rapidly exchanging hydrogen (deuterium) with the solvent, thus the bond being broken is one containing hydrogen (deuterium), and the conjugate acid of the sugar is an intermediate in the mutarotation. We would expect to find the ratio of the rate constants to be 7/3, k_h/k_d .

Procedure

Each group will perform measurements using H_2O and D_2O as solvents. Weigh out 4.500 grams of α -D-glucose and dissolve in 25 mL of water. Fill a polarimeter tube with this solution (as rapidly as possible), and make measurements of the optical rotation of the

solution every 10 minutes for two hours. Make a final reading the next day. Once you have started the measurements in H_2O , follow the above procedure with D_2O .

Calculations

Plot the natural logarithm of the optical rotation ($\ln a$) versus time for each solution. Determine the rate constant for each reaction from the slope of each plot. Determine the ratio $k_{\text{H}}/k_{\text{D}}$. Does this agree with a proposed mechanism?