EXPERIMENT 7

HOW DO YOU KNOW WHICH WAY REACTIONS GO? KINETICS, MECHANISMS, AND THE KINETIC ISOTOPE EFFECT.

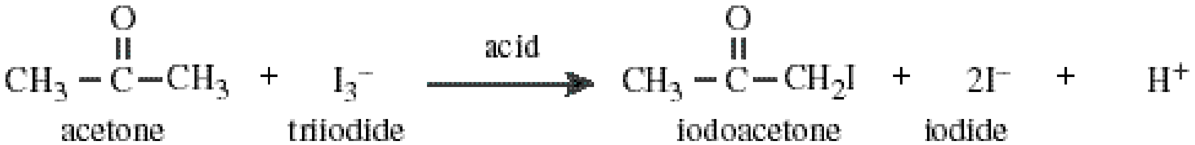
Overview:

- Measurement of the kinetics of a reaction spectrophotometrically.
- Determination of reaction rates, rate constants and reaction orders.
- Concepts include rate-determining step, mechanism, deuterium isotope effect.

I. Introduction

The synthesis of new drugs and other chemicals requires a detailed understanding of chemical reactivity. Chemists skilled in the art of molecular synthesis formulate new molecules based on their understanding of the chemical reactivity of known molecules. To manipulate and control the products and rates of reactions requires a fundamental understanding of reaction mechanisms, i.e. the fundamental steps along the path from reactants to products. Synthetic chemists gain insight through reaction mechanisms that help to identify potential synthetic routes to analogous molecular compounds. In this laboratory experiment, you will use reaction kinetics to examine potential mechanisms for the halogenation of acetone reaction.

In acidic aqueous solution acetone reacts with halogens in a substitution reaction as follows:



$$\underset{\text{acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{\text{triiodide}}{I_3^-} \xrightarrow{\text{acid}} \underset{\text{iodoacetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2I} + \underset{\text{iodide}}{2I^-} + H^+$$

The halogenation of acetone was one of the first reaction mechanisms to be revealed using reaction kinetics.[1] In 1904, A. Lapworth[22] showed that contrary to expectations at the time, the reaction of a halogen with acetone proceeds through an enol intermediate, with the overall reaction mechanism summarized by the following four steps:[2]

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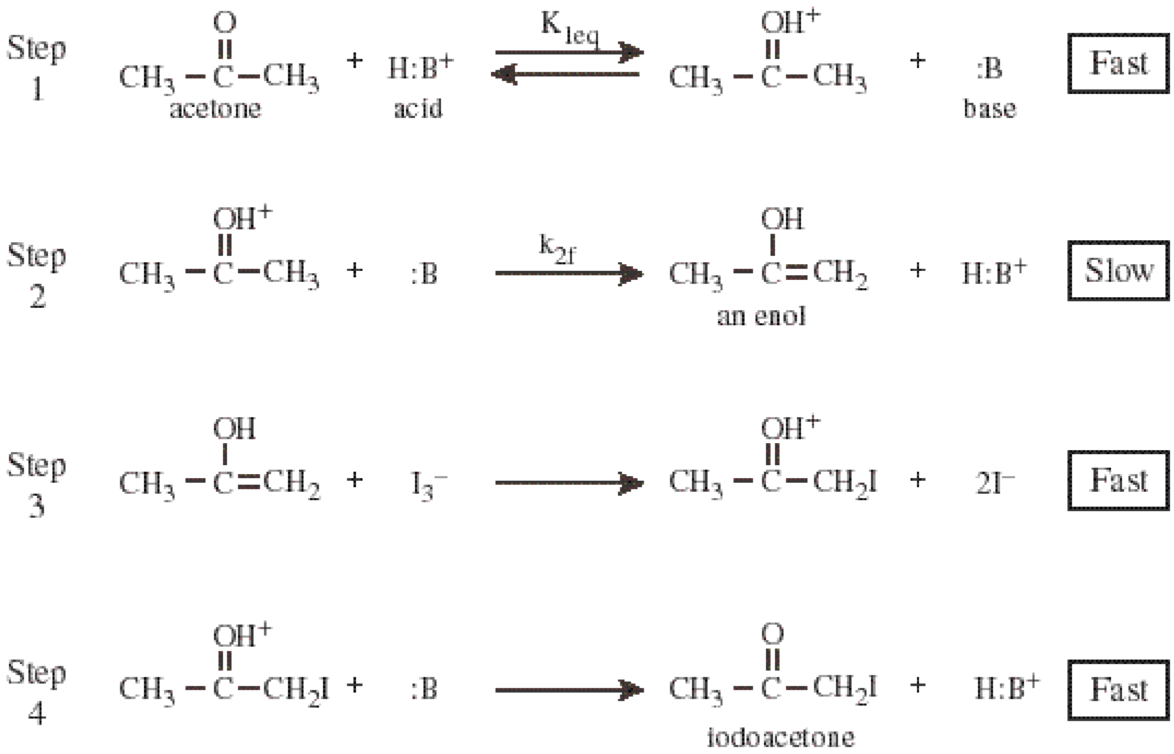
[1] Morrison, R. T. and Boyd, R. N. *Organic Chemistry, Fourth Edition,* Allyn and Bacon, Inc., Boston, MA, 1983.

[2] Lapworth, A. *J. Chem. Soc.,* **35**, 30 (1904).



where :B denotes a base (water, in the current lab), and I_3^- is triiodide ion. It is important to note that an acid, $H{:}B^+$ is needed for the first step to proceed, and that the slow (rate determining step) is the formation of the enol in step 2. Also note that the halogen is not added until after the rate determining step (#2).

You will determine the kinetics of this reaction using a Spec 20 spectrophotometer. As you know, spectrophotometers can be used to measure the concentration of chemical species that absorb light. In the preceding reaction, the only chemical species with an appreciable absorption in the visible region of the spectrum is the halogen. Using the Spec 20, you will follow the halogen concentration and determine the rate of the reaction as,

$$\text{rate} = -\Delta[I_3^-] / \Delta\text{time}$$

By definition the rate of the reaction is always positive and therefore the negative sign in the above equation means that the halogen disappears with time.

In general, the rate of a reaction can depend on the concentration of any chemical species in the reaction mixture. The dependence of the rate on each of these species is summarized in the rate law. For the halogenation of acetone, a general form of the rate law is given below.

$$\text{rate} = -\Delta[I_3^-] / \Delta\text{time} = k\,[H^+]^a\,[CH_3COCH_3]^b\,[I_3^-]^c$$

where k is a constant (called the rate constant), a, b, and c are the orders (powers) with respect to the concentration of each chemical species. In the experiment you will determine the rate constant, k, and order of each chemical species in the rate law. The experimental rate data gathered will be used to either support or refute the mechanism outlined earlier.

In order to determine the rate law, you will use a strategy known as flooding. To simplify the rate expression, all of the chemical species in the rate law except one are added in stoichiometric excess (usually greater than 20:1 excess). For the current experiment $[H^+]$ and $[CH_3COCH_3]$ will be in excess over $[I_3^-]$. The advantage gained from this is that to a very good approximation the concentration of the abundant chemicals do not change. In other words, the rate law simplifies to,

$$\text{rate} = -\Delta[I_3^-]/\ \Delta\text{time} = k'\ [I_3^-]^c,$$

where $k' = k\ [H^+]_0^a\ [CH_3COCH_3]_o^b$ and the o-subscript denotes the initial concentration of the species (which is assumed to be constant).

The reaction order for a species can be found by varying the initial concentration of that species while holding the concentration of the other species constant. For example, if two kinetic runs are implemented, holding all initial concentrations constant except for the acid concentration which is made twice as concentrated in the second run as the first, the order of the reaction can be determined using the ratio of the two runs by the relation $(\text{rate}_2/\text{rate}_1)=\{\ [H^+]_2/[H^+]_1\}^{\ a}$. Since in the current example, the ratio of the acid concentrations is 2, if the second rate was twice the first, the acid concentration is first order (a=1), if the second rate was quadruple the first, the acid concentration would be second order (a=2), etc. Although fractional orders are possible, usually the order of the reactants will be an integer. As you can see, several reactions must be run in order to determine the reaction order of all of the reactants.

A prediction of the proposed mechanism is that the reaction rate should be independent of the initial concentration of halogen used, in other words the reaction is zero order with respect to halogen. (Why?) This is the logical consequence of the addition of the halogen coming after the rate limiting step in the reaction mechanism. How does this affect the rate of the reaction? The rate expression, $\text{rate} = -\Delta[I_3^-]/\ \Delta\text{time} = k'\ [I_3^-]^0 = k'$, says that the change in the triiodide ion concentration with time is a constant. Which means that a plot of $[I_3^-]$ vs time will yield a straight line whose slope is the rate. Orders other than zero would yield a curve rather than a line for the same plot. A second consequence of the mechanism is that the rate should be independent of the amount or the chemical identity of the halogen used as long as step 2 remains rate limiting. That is, whether you use I_3^- or Br_3^-, you should obtain the same rate. These predictions stand in contrast to those based on a mechanism where the halogen reacts directly with the acetone (as was expected before the study of Lapworth) and are part of the evidence which supports the proposed mechanism.

The final piece of data that you will use to determine the mechanism is obtained from the kinetic isotope effect. Deuterium is an isotope of hydrogen with a mass twice that of hydrogen. You will be using 'heavy acetone', CD_3COCD_3, which is acetone that has been synthesized with deuteriums in place of hydrogens. Isotopic substitution is a very useful strategy for determining reaction mechanisms, because the basic chemical identity (electronic configuration) and basic reactivity of the molecule is preserved, but the heavier atoms have *slightly* different bond strengths. **The usual impact of isotopic substitution is to decrease the rate of the reaction for the more massive isotope if a bond involving that isotope is involved in the rate determining step and the bond to the isotopically exchanged atom is stronger in the reactant than in the transition state**. In the proposed mechanism, the rate determining step involves the cleavage of a carbon-hydrogen bond and is therefore predicted to show a deuterium isotope effect. In the ideal case, the exchange of deuterium for hydrogen is predicted to slow the reaction by about a factor of seven.

II. Experimental Procedure

Initially, you will follow the reaction kinetics using the absorbance of I_3^- at a wavelength of 565 nm. Stock solutions of acid and I_3^- will be available in lab. Be sure to record the concentration of each. In addition, acetone and deuterated acetone solutions will be available. Remember to use the potassium iodide (KI) solution for diluting your solutions. Set up one buret with acid and a second with acetone. Use a small graduated cylinder to measure the volumes of the KI and halogen solutions.

Begin by preparing the blank; use the blank to set 100% transmittance (also remember to set the zero). Prepare the first kinetic run by measuring the acetone, KI and I_3^- solution into a test tube and measuring the acid into a clean dry small graduated cylinder. At t=0, mix the solutions and gently agitate. Wipe the outside of the test tube and place it in the spectrophotometer, and record the absorbance (or transmittance) using by starting the computer aided data collection for at least 5 minutes or until an absorbance of near zero. Repeat this procedure for remaining kinetic runs as outlined in the table below.

	Acetone	KI	I_3^-	Acid
Blank	1.0 mL	5.0 mL	0.0 mL	0.0 mL
Abs. Standard	2.0 mL	2.0 mL	2.0 mL	0.0 mL
I_3^- kinetic run 1	2.0 mL	0.0 mL	2.0 mL	2.0 mL
I_3^- kinetic run 2	1.0 mL	1.0 mL	2.0 mL	2.0 mL
I_3^- kinetic run 3	2.0 mL	1.0 mL	1.0 mL	2.0 mL
I_3^- kinetic run 4	2.0 mL	1.0 mL	2.0 mL	1.0 mL
Deuterium run	2.0 mL*	0.0 mL	2.0 mL	2.0 mL

*Deuterated acetone.

Prelab Questions

Answer these questions in your laboratory notebook. Hand in the original to your TA. Be sure to include your name, and section number. You must show all of your work to receive full credit.

1. In the mechanism outlined in this handout, the first reaction is given as a fast equilibrium with products identical to the reactants in step 2. Write the equilibrium expression (K_{1eq}) for the 'pre-equilibrium' depicted in step 1. (3 pts)

2. Because the chemical equations given in the reaction mechanism represent elementary chemical steps, the rate law is directly related to the balanced chemical reactions. Assume a forward rate constant of k_{2f} for the reaction depicted in step 2; write the rate law in terms of k_{2f} and the concentrations of reactants. (3 pts)

3. Using the results of 1 and 2, write the rate law of step 2 in terms of K_{1eq}, k_{2f}, the acetone concentration $[CH_3COCH_3]$, and the acid concentration $[H{:}B^+]$. This is your predicted rate law for the experiment. What is the order of each of the following: $[CH_3COCH_3]$, $[H{:}B]$, and $[I_3^-]$. (4 pts)

4. Experimental Purpose and Procedure (5 pts)