

F. Experiment #6, Kinetics Study of the Iodination of Acetone

Objectives:

1. Experimentally determine the rate law for the iodination of acetone.
2. Investigate the use of the steady-state approximation in kinetics studies.
3. Measure and record the reaction rate by the use of absorption spectroscopy.

Background:

Rate Law

We will begin this lab with a discussion of the general description of reactions, rates and rate laws. We will discuss a general reaction:



As the reaction occurs, the concentrations of the reactants and the products will change. The rate of the reaction can be characterized by any of the following:

$$rate = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{d} \frac{d[D]}{dt} = \frac{1}{e} \frac{d[E]}{dt} \quad (2)$$

The above equation defines the reaction rate. The reaction rate is defined in terms of the rate of change of concentration for any of the reaction components, divided by the stoichiometric coefficient for that component. Stoichiometric coefficients are positive for products and negative for reactants.

The reaction rate is dependent on the concentrations of chemical species involved in the reaction. In general the rate of a reaction depends on the concentrations of species as follows:

$$rate = k[A]^p[B]^q \quad (3)$$

This equation is the **rate law** of the reaction. The proportionality constant, k , is known as the **rate constant** of the reaction. In general, the rate constant depends on temperature, commonly increasing with temperature. The

exponents in the rate law are often small integers (positive or negative) or simple fractions. These exponents are determined experimentally.

Reaction Order

The exponent on the concentration terms in Equation (3) is the order of the reaction with respect to each component of the reaction. For example, p is the order of the reaction with respect to the concentration of component A. If p is zero, the rate of reaction is independent of the concentration of A. The sum of the exponents is the overall **order of the reaction**.

Initial Rate Method

By measuring the change in concentration of one of the components of the reaction system with time, one can collect rate information. This data can be used to determine the initial rate of the reaction, the rate early in the reaction. By taking the ln of Equation (3) one gets an expression relating the ln of the rate to the sum of the ln of the rate constant and the ln of the concentrations of the reaction components:

$$\ln(\text{rate}) = \ln k + p \ln[A] + q \ln[B] \quad (4)$$

The ln of the concentrations of the individual reaction components are multiplied by the reaction order for that component. By measuring the initial rate of the reaction while changing the initial concentration of one of the reaction components, one can determine the order of the reaction with respect to that component. This is done by plotting the ln of the initial reaction rate versus the ln of the initial concentration of the varying component (all other initial concentrations are held constant). This should result in a straight line of slope equal to the order for that component. This process can be repeated, varying concentrations of other individual components in the reaction system.

Iodination of acetone

When iodine is mixed with acetone, the following reaction occurs:



An analogous reaction occurs between bromine and acetone. The reaction is quite slow in the pH range of 4-7, but it occurs quite rapidly if the pH is below 3 or above 8. This implies an acid or base dependence.

The rate law for a reaction cannot be predicted from the balanced equation for the reaction. The rate law can only be determined experimentally. This reaction has been found to be catalyzed by the hydrogen ion. The reaction rate increases with the concentration of H^+ in acidic solution or with the concentration of OH^- in basic solution. The rate law is assumed to have the form:

$$rate = -\frac{d[CH_3C(O)CH_3]}{dt} = -\frac{d[I_2]}{dt} = k[CH_3C(O)CH_3]^p [I_2]^q [H^+]^r \quad (6)$$

Where k is the rate constant and $[A]$ represents the concentration of species A in moles/liter. The exponents, p , q , and r indicate the order of the reaction with respect to acetone, iodine, and hydrogen ion, respectively.

It has been found that the rate of halogenation of acetone is independent of the concentration of halogen, except at very high acidities. The rates of reaction with the different halogens (chlorine, bromine and iodine) are identical, within a few percent. These facts are consistent with the mechanism.

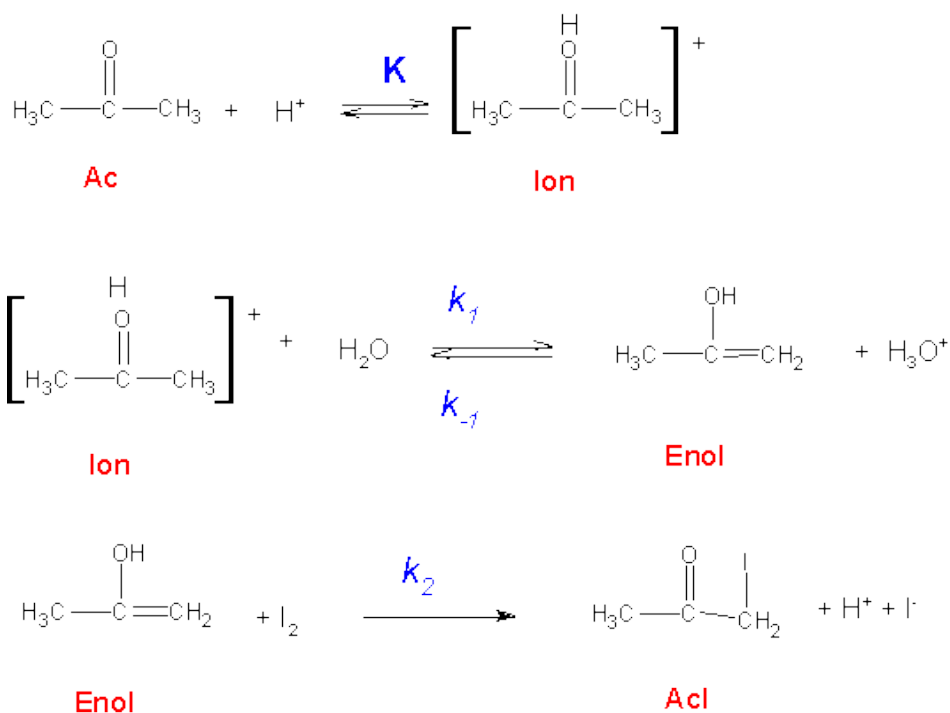


Figure 1: acetone iodination reaction mechanism

Since ketones are very weak bases, the equilibrium in the first reaction above is unfavorable for the formation of the ion. Under these circumstances $[\text{Ion}] = K[\text{Ac}][\text{H}^+]$, where K is the equilibrium constant for this reaction.

The rate equations for enol (Enol) and product (AcI) are, according to the mechanism:

$$\begin{aligned}
 \frac{d[\text{Enol}]}{dt} &= k_1[\text{Ion}] - \{k_{-1}[\text{H}^+] + k_2[\text{I}_2]\}[\text{Enol}] \\
 \frac{d[\text{AcI}]}{dt} &= k_2[\text{I}_2][\text{Enol}]
 \end{aligned} \tag{7}$$

These rate equations may be solved for $d[\text{AcI}]/dt$ under steady-state conditions by letting $d[\text{Enol}]/dt = 0$ and substituting $[\text{Int}] = K[\text{Ac}][\text{H}^+]$. This results in:

$$\frac{d[\text{AcI}]}{dt} = \frac{k_1 k_2 K [\text{Ac}][\text{H}^+][\text{I}_2]}{k_{-1}[\text{H}^+] + k_2[\text{I}_2]} \quad (8)$$

This equation can be simplified if the enol which is formed in the second step reacts more rapidly with the halogen than with hydrogen ions; that is, $k_2[\text{I}_2] \gg k_{-1}[\text{H}^+]$.

$$\frac{d[\text{AcI}]}{dt} = k_1 K [\text{Ac}][\text{H}^+] \quad (9)$$

This mechanism suggests that the over-all reaction is first-order in acetone and acid, but independent of the concentration of halogen.

Procedure:

Measuring the reaction rate by absorption spectroscopy

The iodination of acetone is a particularly convenient and interesting reaction to study kinetically. The progress of the reaction is easily followed by directly observing the decrease in iodine concentration spectrophotometrically at a wavelength where none of the other reagents has significant absorption.

You will need to come up with a procedure for this lab using the Ocean Optics® UV-VIS Spectrometer.

Reminder: Beer-Lambert law

The Beer-Lambert law describes the absorption of light in matter. It states that the intensity of light after it passes through a substance is logarithmically related to the initial intensity of light. This relation depends on the product of the absorption coefficient of the substance, α and the distance the light travels through the material, l .

$$I = I_0 \cdot 10^{-\alpha l} \quad (10)$$

Here I is the measured light intensity and I_0 is the initial light intensity. The absorbance, A , of light through a substance is defined as $A = -\log(I/I_0)$. In liquids, the absorption coefficient is a product of the molar absorptivity of the absorber, ϵ , and the concentration c of absorbing species, so that:

$$A = \alpha l = \epsilon cl \quad (11)$$

Once ϵ and l are known, the Beer-Lambert law may be used to calculate the concentration of a solution by absorption spectroscopy.

Calculating the reaction rate

As will be confirmed in this experiment, the reaction is zero order in iodine, i.e., q in equation (6) is zero. This result provides a straightforward application of the method of initial rates wherein the acetone and acid are present in large excess while the iodine is used in small concentrations to limit the extent of reaction. The small amount of iodine is completely consumed while the other reactants remain at an essentially constant concentration. Since the reaction rate is independent of the iodine concentration, the rate is constant until all of the iodine is consumed. Under these conditions:

$$rate = -\frac{d[I_2]}{dt} = k[CH_3C(O)CH_3]^p[H^+]^r = \text{constant} \quad (12)$$

A plot of $[I_2]$ versus time is a relatively straight line whose slope is the reaction rate.

It is necessary to confirm that the exponent q is indeed zero. To do this the results of at least four experiments in which only the initial $[I_2]$ differ, while the initial $[CH_3C(O)CH_3]$ and $[H^+]$ are unchanged must be analyzed. The slope of the plot of the $\ln()$ of the rate of reaction versus the $\ln()$ of $[I_2]$ is the reaction order for I_2 , q .

In order to get good results, at least four experiments with different initial $[CH_3C(O)CH_3]$, and three experiments with different initial $[H^+]$ should be performed. The order of the reaction p is determined from a plot of the $\ln()$ of the rate of reaction versus the $\ln()$ of the initial $[CH_3C(O)CH_3]$. The slope of this plot is the reaction order for $CH_3C(O)CH_3$, p . The order of the reaction r is determined from a plot of the $\ln()$ of the rate of reaction versus the $\ln()$ of the initial $[H^+]$. The slope of this plot is the reaction order for H^+ , r .

The rate constant for the reaction can now be determined by the application of equation (6). A plot of the rate of reaction versus the product

$[\text{CH}_3\text{C}(\text{O})\text{CH}_3]_0^p [\text{H}^+]_0^r$ should be linear, and its slope is the rate constant for the reaction.

Report:

Make sure to include, in addition to the normal sections, a detailed description of your procedure in a separate section titled “Procedure”.