

## CHEMICAL KINETICS: IODINATION OF ACETONE

### OBJECTIVE:

To study the rates of acid-catalyzed iodination of acetone and the relationship with a proposed mechanism.

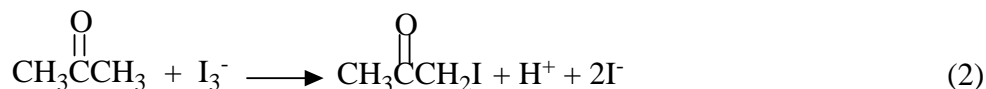
### THEORY:

This reaction was studied by Lapworth in 1904 and was one of the first mechanisms to be studied kinetically. It was found that if a dilute solution of iodine in acidic aqueous acetone is allowed to stand at room temperature a slow reaction occurs represented by the equation,

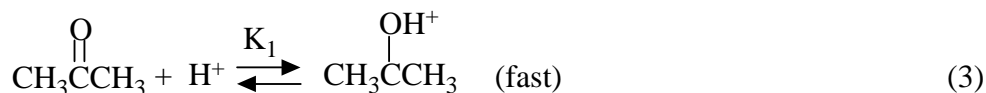


It may be followed by removing aliquots, adding excess potassium iodide solution and titrating the iodine remaining with sodium thiosulfate solution. If the concentration of the acid catalyst is considerably greater than that of the iodine solution the reaction is of zero order, i.e. the rate of the reaction is constant with time and does not depend upon the concentration of iodine or acetone. The basic theoretical principle used in interpreting this fact is that the kinetic results describe what is happening in the rate determining step of the reaction. Hence the logical conclusion is that the rate-determining step does not involve iodine.

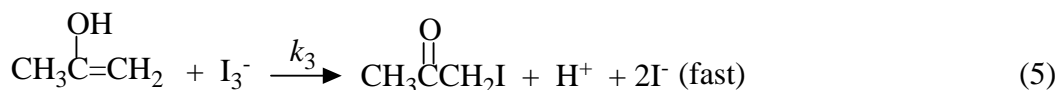
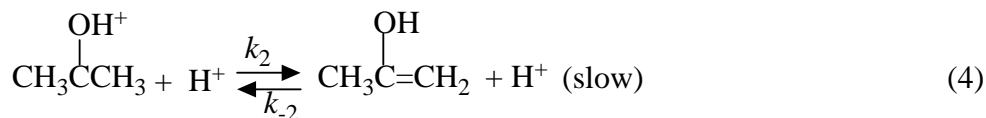
It has been proposed that the net reaction:



proceeds via the following mechanism in acidic solutions:



where  $K_1$  = equilibrium constant



where  $k_2$ ,  $k_{-2}$ , and  $k_3$  are rate constants.

Then, it can be shown that, if  $k_3[\text{I}_3^-] \gg k_2[\text{H}^+]$ , the rate is

$$\frac{-d[\text{acetone}]}{dt} = \frac{-d[\text{I}_3^-]}{dt} = k_2 K_1 [\text{H}^+] [\text{acetone}] \quad (6)$$

One of the objectives of this experiment is to test this proposed mechanism.

Derivation of the rate expression from the proposed mechanism:

Using the steady-state treatment for  $\text{CH}_3\overset{\text{OH}}{\text{C}}=\text{CH}_2$ ,

$$\frac{d[\text{CH}_3\overset{\text{OH}}{\text{C}}=\text{CH}_2]}{dt} = k_2 [\text{CH}_3\overset{\text{OH}^+}{\text{C}}\text{CH}_3] - k_2 [\text{CH}_3\overset{\text{OH}}{\text{C}}=\text{CH}_2] [\text{H}^+] - k_3 [\text{I}_3^-] [\text{CH}_3\overset{\text{OH}}{\text{C}}=\text{CH}_2] = 0$$

therefore  $k_2 [\text{CH}_3\overset{\text{OH}^+}{\text{C}}\text{CH}_3] = [\text{CH}_3\overset{\text{OH}}{\text{C}}=\text{CH}_2] (k_2 [\text{H}^+] + k_3 [\text{I}_3^-])$

from step 1:  $[\text{CH}_3\overset{\text{OH}^+}{\text{C}}\text{CH}_3] = K_1 [\text{H}^+] [\text{CH}_3\text{COCH}_3]$

therefore  $k_2 K_1 [\text{H}^+] [\text{CH}_3\text{COCH}_3] = [\text{CH}_3\overset{\text{OH}}{\text{C}}=\text{CH}_2] (k_2 [\text{H}^+] + k_3 [\text{I}_3^-])$

from step 3:  $\text{Rate} = \frac{-d[\text{I}_3^-]}{dt} = k_3 [\text{I}_3^-] [\text{CH}_3\overset{\text{OH}}{\text{C}}=\text{CH}_2] = \frac{k_3 [\text{I}_3^-] k_2 K_1 [\text{H}^+] [\text{CH}_3\text{COCH}_3]}{k_2 [\text{H}^+] + k_3 [\text{I}_3^-]}$

Then if  $k_3 [\text{I}_3^-] \gg k_2 [\text{H}^+]$   $\text{Rate} = \frac{-d[\text{I}_3^-]}{dt} = k_2 K_1 [\text{H}^+] [\text{CH}_3\text{COCH}_3]$

and the reaction is pseudo zero order in  $[\text{I}_3^-]$ .

The rate of the reaction in our experiment will be followed by spectrophotometry rather than by taking aliquots and titrating using standardized sodium thiosulfate solution. Since the  $\text{I}_3^-$  ion absorbs strongly in the visible region we must first determine the optimum wavelength in the absorption spectrum of the  $\text{I}_3^-$  ion. To calculate the proportionality constant ( $\epsilon$ ) which will be needed later, one assumes Beer's Law at the optimum wavelength:

$$\text{Absorbance} = A = (\epsilon \ell) [\text{I}_3^-] \quad (7)$$

The plan is to "flood" the reaction with large excess of both acetone and hydrogen ions. As a result, if the proposed mechanism is correct, one has the following consequences:

(1) The observed rate should be pseudo-zero order

$$-d[I_3^-]/dt = k_{\text{obs}} \quad (8)$$

The integrated rate law is  $-[I_3^-]_t = k_{\text{obs}}t + \text{constant}$  (9)

at  $t = 0$  the constant =  $-[I_3^-]_0$  and therefore

$$[I_3^-]_t = [I_3^-]_0 - k_{\text{obs}}t \quad (10)$$

However since the absorbance  $A = (\epsilon\ell)[I_3^-]$  from Eq.(7) then Eq.(10)becomes

$$A_t = A_0 - k_{\text{obs}}(\epsilon\ell)t \quad (11)$$

where  $k_{\text{obs}} = k_2K_1[H^+][\text{acetone}]$  and is a constant for each run.

(2) The values of  $k_2K_1$  obtained from  $k_{\text{obs}}/[H^+][\text{acetone}]$  should be the same for all the runs.

### **PROCEDURE:**

#### Absorption of the $I_3^-$ ion

At 450 nm, measure the absorbance of 0.00020, 0.00040, 0.00060, 0.00080, and 0.0010 M solutions of  $KI_3$ . Plot A versus  $[I_3^-]$  and calculate the constant ( $\epsilon\ell$ ).

#### Kinetic Runs

For each run, pipette  $x$  mL of 1 M HCl,  $y$  mL of 0.01 M  $KI_3$  into a 250 mL volumetric flask. Add water to about 5 mL below the mark. As  $z$  mL of acetone is pipetted into the flask, start a stop watch. Add water to the mark and shake well. Fill a cuvette with the solution and follow the absorption at 450 nm. As the spectrophotometer is most accurate in the absorbance range 0.1 to 1.0, data with absorbance greater than 1.0 can be discarded. A convenient way of following the absorbance as a function of time is to record the absorbance using the strip chart recorder.

<u>Run No.</u>	<u>1M HCl x mL</u>	<u>0.010M <math>KI_3</math> y mL</u>	<u>Acetone z mL</u>
1	25	20	2
2	50	20	2
3	25	10	1
4	25	20	4

The density and molecular weight of acetone are  $0.7908 \text{ g/cm}^3$  (at  $20^\circ\text{C}$ ) and  $58.08 \text{ g/mole}$ . Complete the following concentration table.

<u>Run No.</u>	$[\text{H}^+]$	$[\text{I}_3^-]$	[acetone]
1			
2			
3			
4			

For each run, plot  $A_t$  versus  $t$ , determine the slope, and calculate  $k_{\text{obs}}$  as well as  $k_2K_1$ . Verify that the results fit the rate equation(6).

### QUESTIONS:

1. Calculate the half-life for this reaction under the conditions you used. Is it the same for all four runs? If not, explain why?
2. What would you predict the rate of deuterium exchange to be for acetone under acidic conditions similar to this experiment?
3. If the reaction is carried out with a small initial amount of acid the phenomenon of autocatalysis is observed. What is this phenomenon of autocatalysis?

### REFERENCES:

1. Benson, S.W., The Foundations of Chemical Kinetics, McGraw-Hill, 1960. Pages 569-573.
2. Knight, A.R., Introductory Physical Chemistry, Prentice-Hall 1970, Chapter 6.
3. Latham, J.L., Elementary Reaction Kinetics, Butterworths, 1964
4. Harris, G.M., Chemical Kinetics, D.C.Heatch and Company, 1966