

## EXPERIMENT 6

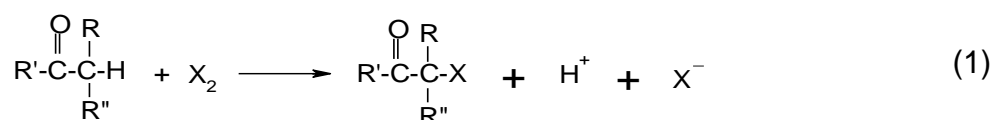
## KINETICS OF CHEMICAL REACTION - IODINATION OF CYCLOHEXANONE

## Background

Many reactions that follow simple rate laws actually occur through a series of steps. These steps are called elementary reactions because they cannot be broken down further into simpler reactions. The sequence of elementary reactions that add up to give the overall reaction is called the mechanism of the reaction.

A mechanism is a hypothesis about the elementary steps through which chemical change occurs. Sometimes the elementary steps can be studied in isolation, but in most cases they cannot be easily separated. Sometimes more than one mechanism could be proposed for a particular chemical reaction, and evidence of the correct mechanism is often indirect. A valid mechanism must agree with all the facts about the kinetics and knowledge about the reactants and intermediates involved. It must be able to explain the rate law of the backward as well as the forward reaction.

In general, the halogenation of a ketone can be represented as follow:

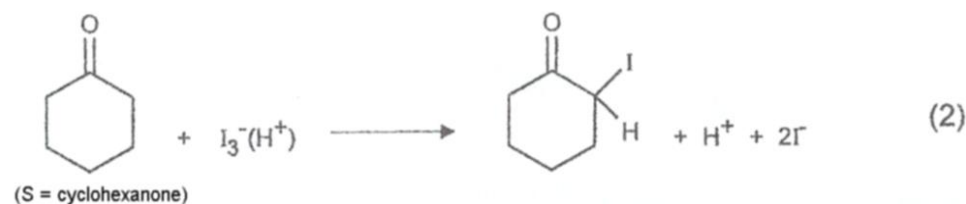


where X=halogen atom. This reaction could be catalyzed by  $\text{H}^+$  in acidic solution or by  $\text{OH}^-$  in alkaline solution.

## Iodination of cyclohexanone

In this experiment, the rate of iodination of cyclohexanone in an aqueous medium is being measured. To increase the amount of iodine in the solution, it is necessary to convert to its more soluble complex ion  $\text{I}_3^-$  by addition of excess of iodide ion:  $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$ .

The overall reaction of iodination of cyclohexanone in an aqueous solution with excess  $\text{I}^-$  ion can be represented as follows



Following the rate law of chemical kinetics, the differential rate equation for the reaction could be written in the following form

$$-\frac{d[S]}{dt} = -\frac{d[I_3^-]}{dt} = k [S]^a [I_3^-]^b [H^+]^c \quad (3)$$

where  $k$  = rate constant;  $a$ ,  $b$  and  $c$  are the orders of reaction with respect to  $S$ ,  $I_3^-$  and  $H^+$  respectively.

This experiment is carried out to determine the value of  $k$ ,  $a$ ,  $b$  and  $c$ , and to suggest a mechanism which agrees with the rate equation that has been obtained.

As the  $I_3^-$  ion is the only colored species in the reaction mixture, a spectrophotometer could be employed to measure the change in its concentration, by using the Beer-Lambert Law

$$A(I_3^-) = \epsilon l [I_3^-] \quad (4)$$

where  $A$  = absorbance,  $\epsilon$  = molar absorption coefficient,  $[I_3^-]$  = concentration and  $l$  = optical path length, that is, the distance traveled by the light through the solution. The most suitable wavelength for the measurement of  $I_3^-$  ion concentration is 565 nm.

*[Subsequently the absorbance  $A$  refers to that due to  $I_3^-$ , measured at 565 nm].*

Deriving from equation (4),

$$[I_3^-] = \epsilon^{-1} l^{-1} A \quad (5)$$

where  $\epsilon^{-1} l^{-1}$  may be treated as a single constant, and is calculated from the absorbance measurement made during Spectrophotometer calibration.

The progress of reaction (3) could be monitored by measuring the change in the concentration of  $I_3^-$  with reaction time.

However, the rate of change in the values of solution absorbance,  $-dA/dt$ , can be correlated to the rate of change in the concentration of  $I_3^-$  by equation (6).

$$-\frac{dA}{dt} = -\epsilon l \frac{d[I_3^-]}{dt} \quad (6)$$

The general rate equation (3) can therefore be written as

$$-\frac{dA}{dt} = k\epsilon l [S]^a [I_3^-]^b [H^+]^c \quad (7)$$

A direct comparison between rate and concentration can be done approximately by taking as a measure of the derivative  $dA/dt$  the corresponding ratio of finite increments  $\Delta A/\Delta t$ .

Then by making a run at each of two different initial concentrations of any one component, say the cyclohexanone, keeping the other concentrations constant, the data may be used to determine the order of reaction with respect to that component.

Let the two rates and corresponding initial concentration be  $(dA/dt)_1$ ,  $(dA/dt)_2$ , and  $[S]_1$ ,  $[S]_2$ , respectively. Then

$$-\left(\frac{dA}{dt}\right)_1 = k [I_3^-]^b [H^+]^c [S]_1^a \quad (8)$$

$$-\left(\frac{dA}{dt}\right)_2 = k [I_3^-]^b [H^+]^c [S]_2^a \quad (9)$$

From equations (8) and (9), dividing and taking logarithms, we can obtain

$$a = \frac{\log \frac{(dA/dt)_1}{(dA/dt)_2}}{\log \frac{[S]_1}{[S]_2}} \quad (10)$$

or  $a = \{\log (dA/dt)_1 - \log (dA/dt)_2\} / \{\log [S]_1 - \log [S]_2\}$ .

An exactly analogous procedure yields the values of  $b$  and  $c$ .

### Experimental Procedure

The following solutions are to be prepared from the stock solutions:

	Volume of stock solution used /cm <sup>3</sup>			
	I	II	III	IV
Cyclohexanone	20	20	20	14
HCl	10	10	6	10
Distilled Water	14	16	20	22
KI <sub>3</sub>	6	4	4	4

[Cyclohexanone] stock = 0.230 mol dm<sup>-3</sup>

[HCl] stock = 0.500 mol dm<sup>-3</sup>

[KI<sub>3</sub>] = 0.0360 mol dm<sup>-3</sup>

Mix the acid, ketone and water together in a 100 cm<sup>3</sup> conical flask. Label the flask and place in the 303 K constant temperature bath and allow the flask

and its content to equilibrate for at least 15 minutes. Thermostat the  $KI_3$  stock solution as well.

After thermal equilibrium has been attained, the reaction is started by pipetting the required amount of the  $KI_3$  solution into the flask. As soon as the pipette has drained, the timer is started and the mixture mixed thoroughly and returned to the bath. Immediately, a sample is transferred from the flask to a spectrophotometer sample cell (using a dropper) and its absorbance measured. The sample cell is then emptied, rinsed with distilled water, and dried. Further samples are taken and measured at intervals of 2 minutes, until sufficient points are obtained for giving a good plot of absorbance  $A$  versus time.

Carry out the same procedure each of the mixture I, II, III and IV. Determine the gradient of the each plot of absorbance  $A$  versus time.

### Operation of the Spectrophotometer

The operation manual can be obtained from the lecturer-in-charge or the Laboratory Assistant. Make sure you know how to operate the instrument (you can ask the lecturer/demonstrator/lab. assistant for help).

Make sure you measure the absorbance of  $KI_3$  solution of  $0.00360 \text{ mol dm}^{-3}$  a few times to obtain the best average value for  $\epsilon l$ .

### Calculations and Conclusion

The values of  $dA/dt$  for each experiment may be obtained readily from the slopes of graphs of absorbance  $A$  as a function of time for each experiment. The slopes should be determined by a graphical method, together with the uncertainty analysis.

The uncertainties in the values of  $\log dA/dt$  and  $\log$  (concentration) are then used to determine the uncertainties in the reaction orders obtained.

Using the value of  $\epsilon l$  which you have determined, the rate constant  $k$  can be calculated using equation (7) for each of the four runs (I)-(IV). The average value and its standard deviation are then obtained. The mean value should be compared with the literature value.

There are three mechanisms of reaction being proposed for the iodination of cyclohexanone (Schemes A, B and C). Show whether the form of the rate equation which you have determined is consistent with any of these. If so, which step of the chosen mechanism is the rate-determining one?

Are your results consistent with the observation that the rate of bromination of ketones is exactly the same as the rate of iodination?

## References:

1. G.W.Barrow, "Physical Chemistry", 2<sup>nd</sup> Ed., McGraw-Hill, 1966
2. R.T.Morrison & R.N.Boyd, "Organic Chemistry", Allyn & Bacon, 1959
3. P.W.Atkins, "Physical Chemistry", 4<sup>th</sup> Ed., Oxford, 1994
4. I.N.Levine, "Physical Chemistry", 4<sup>th</sup> Ed., McGraw-Hill, 1995
5. R.A.Alberty & R.J.Silbey, "Physical Chemistry", 2<sup>nd</sup> Ed., John Wiley 1997.

## PROPOSED MECHANISMS OF IODINATION OF CYCLOHEXANONE

