LABORATORY SESSION 5

Kinetic study of the reaction between iodine and acetone catalyzed by acid

Material
1 x 500 mL volumetric flask
1 x 100 mL volumetric flask
1 x 250 mL volumetric flask (shared)
1 x 250 mL volumetric flask
7 x 100 mL Erlenmeyer flasks
1 x 3 mL volumetric pipette
1 x 5 mL volumetric pipette
1 x 10 mL volumetric pipette
1 x 15 mL volumetric pipette
1 x 10 mL graduated pipette
1 x 50 mL burette
1 x 250 mL Erlenmeyer flask
2 x 100 mL beakers
1 x 50 mL beaker
1 x 100 mL test tube
1 thermostatic bath with thermometer
1 x 1 L topaz bottle
1 stirrer / 1 magnet / 1 weighting glass
1 chronometer

Products
Sodium thiosulfate pentahydrate
Acetone
Hydrochloric acid
Sodium acetate trihydrate
Sodium hydroxide 1M
Phenolphthalein
Starch indicator
Iodine 0.06 M

Objectives

1. To sequentially determine the kinetic parameters: partial orders, apparent rate constants and absolute rate constants.
2. To apply the Ostwald isolation method.

Theoretical background

In water solution, the acetone iodation reaction is slow but can be accelerated when catalyzed in acid medium:

$$CH_3-CO-CH_3+I_2\xrightarrow{H^+}CH_3-CO-CH_2I+HI$$

This reaction occurs via a three-step mechanism: the first (1) and second steps (2) are the keto-enol equilibrium in acid medium, while the third step (3) is the reaction between the enol and the iodine. From a kinetic point of view, steps (1) and (3) are fast but step (2) is slow. Step (2) is therefore the determining step in the mechanism.

$$CH_3-CO-CH_3+H^+\xleftrightarrow{(1)}CH_3-COH^+-CH_3\xleftrightarrow{(2)}CH_3-COH=CH_2+H^+$$

$$CH_3-COH=CH_2+I_2\xrightarrow{(3)}CH_3-CO-CH_2I+HI$$

The reaction rate can be expressed as:

$$v=-\frac{d[I_2]}{dt}=k[\text{Acet}]^a[H^+]^b[I_2]^c \qquad (1)$$

where "k" is the absolute rate constant, and "a", "b" and "c" are the partial orders with respect to acetone (Acet), protons and iodine, respectively.

In this experimental set up, as the concentration of acetone and acid will remain constant during the reaction, the kinetic can be followed with respect to the iodine (the test reagent or indicator). We will therefore be using the Ostwald isolation method. To do so, we use a very high initial concentration of acetone and, since HCl is the catalyzer (the number of moles at any given moment is practically equal to the initial number), the concentrations will remain constant throughout the reaction:

$$\left([H^+]_0, [Acet]_0 \cong [H^+], [Acet] \cong cts\right)$$

Bearing this in mind, the reaction will be of pseudo-order "c" and the rate expression can be simplified as:

$$v = k_{ap}\,[I_2]^c \qquad (2)$$

where the apparent constant is:

$$k_{ap} = k[Acet]_0^a[H^+]_0^b \qquad (3)$$

Given that iodine is not involved in the determining step, the rate will not depend on the concentration of iodine, i.e. the rate will be of zero order with respect to iodine (c=0), and:

$$v = k_{ap} \qquad (4)$$

To follow the evolution of iodine concentration, sample aliquots will be extracted from the reaction. The reaction will then be stopped in each aliquot and the iodine concentration will be determined by titration with sodium thiosulfate, in accordance with the following reaction:

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Since the reaction is catalyzed by acid, the reaction will stop when the catalyzer is removed by adding a base or basic salt. By conducting several experiments in which only the concentration of one of the excess reagents (acetone or acid) is varied, we can measure how these reagents affect the rate reaction and so calculate their partial orders of reaction.

Solutions

1. Iodine 0.06 M (I_2) (already prepared).
2. NaOH 1 M standardized (already prepared).
3. Sodium thiosulfate ($Na_2S_2O_3$) 0.005 M, 500 mL. To avoid exposure to light, the solution must be transferred to a topaz bottle after preparation.
4. HCl 1.2 M, 250 mL (to be shared with all your classmates at the table), from the commercial HCl solution (in the laboratory fume cupboard).

5. Sodium acetate (AcNa) 2.5 % in weight, 250 mL. (**Warning**: sodium acetate is trihydrate).

Experimental procedure

1. Connect the thermostatic bath at 25 ºC.
2. Prepare solutions 3 (shared) and 4.
3. Titrate the HCl solution (solution 4; take a 10 mL sample) with NaOH 1M (solution 2). Each pair will perform one titration and share their results.
4. Three series of experiments are carried out where, compared two by two, the concentration of one of the reagents, acid or acetone, is varied and that of the other is kept constant. As described below.

Series 1: acetone 5 mL and hydrochloric acid 5 mL 1.2 M

5. In a 100 mL volumetric flask, prepare the mixture for the reaction in the following order: water 50 mL + HCl 5 mL + acetone 5 mL. Adjust the volume with water.
6. Transfer this solution to an Erlenmeyer flask with a magnetic stirrer and insert the flask into the thermostatic bath onto the stirrer.
7. Prepare 7 Erlenmeyer flasks with 10 mL of sodium acetate 2.5 %.
8. Fill the burette with sodium thiosulfate and adjust the volume.
9. When thermal equilibrium is reached (after roughly 5 minutes), add 10 mL of I_2 (solution 1) to the Erlenmeyer flask. Start the chronometer (**t = 0**) when the pipette is half empty.
10. Two or three minutes later, take a sample aliquot of 10 mL, V_{aliq}, and drop it into an Erlenmeyer flask with sodium acetate 2.5 %. Record the time at which the volume in the pipette is halved (t = length of time at which the reaction is stopped).
11. Titrate the sample with $Na_2S_2O_3$ 0.005 M until the color fades. Warning! Before the titration ends, add the starch indicator.
12. Take sample aliquots of 10 mL every **eight minutes** and titrate as indicated in point 11 until all samples (seven) are taken.

Series 2: acetone 15 mL and hydrochloric acid 3 mL

Repeat the experiment as indicated for Series 1, taking sample aliquots every **6 minutes**.

Series 3: acetone 15 mL and hydrochloric 5 mL

Repeat the experiment as indicated for Series 1, taking sample aliquots every **4 minutes**.

Note: Remember that all residues must be disposed of in suitable containers when you finish the experiments.

Experimental results: data presentation

1. Clearly show the calculations you performed to prepare the various solutions. Indicate the theoretical masses or volumes and the real masses or volumes and recalculate all concentrations (Table 1).
2. Present the titration data for the hydrochloric acid solution with NaOH and calculate the concentration of HCl with its random error (Table 2).
3. Tabulate the results of each series, i.e. the times of the reaction and the volume of thiosulfate consumed (Table 3).

Data treatment and discussion

WARNING!!! Very important: show the UNITS for all magnitudes

1. Verify that the reaction is of zero order with respect to iodine (c=0). To do so, the integrated rate law of zero order must be represented, where the iodine concentration changes linearly over time, according to:

$$[I_2]_t = [I_2]_o - k_{ap}t \qquad (5)$$

All series must be represented on the same graph.

OPTIONAL: Instead of this equation, we can use an equivalent equation based on the volume of thiosulfate consumed in the titration of the aliquot sample (V_{thios}), since the stoichiometric ratio between the number of moles of iodine and the number of moles of thiosulfate is $n_{I_2} = 1/2\, n_{tios}$. The iodine concentration at a given instant t, $[I_2]_t$, is therefore directly proportional to the volume of thiosulfate, according to:

$$[I_2]_t = \frac{1}{2}\frac{[S_2O_3^{2-}]V_{thios(t)}}{V_{I_2}} = AV_{thios(t)} \qquad (6)$$

where A is a constant whose value is $A = \frac{1}{2}[S_2O_3^{2-}]/V_{I_2}$. Replacing expression (6) in (5) we obtain:

$$V_{thios(t)} = V_{thios(o)} - k'_{ap}t \qquad (7)$$

where

$$k'_{ap} = \frac{k_{ap}}{A} \qquad (8)$$

and $V_{thios(0)}$ is the volume of thiosulfate that would be consumed in order to titrate an aliquot when the reaction begins, i.e. t = 0.

If the volume of thiosulfate is represented over time for each series and the points have a linear fit, it is verified that the reaction is of zero order with respect to iodine.

2. Calculate the apparent rate constants.

   From the linear fit in point 1 above (equation 5), $\mathbf{k'_{ap,i}}$ will be obtained from the slope for each series.

3. Calculate the initial concentrations for acetone and acid for each series.

4. Calculate the partial orders with respect to acetone (a) and acid (protons) (b).

   To do so, apply equation (3) to the series taken in pairs so that the concentration of one reagent is the same.

   4.1. [HCl] equal in series 1 and 3:

$$\frac{series\ 1}{series\ 3} \Rightarrow \frac{k_{ap,1}}{k_{ap,3}} = \left(\frac{[Acet]_{o,1}}{[Acet]_{o,3}}\right)^a$$

, take logarithms: $\ln\left(\frac{k_{ap,1}}{k_{ap,3}}\right) = a\ln\left(\frac{[Acet]_{o,1}}{[Acet]_{o,3}}\right)$ and isolate:

$$\boxed{a = \frac{\ln k_{ap,1} - \ln k_{ap,3}}{\ln[Acet]_{o,1} - \ln[Acet]_{o,3}}} \qquad (9)$$

   4.2. [Acet] equal in series 2 and 3:

$$\frac{series\ 2}{series\ 3} \Rightarrow \frac{k_{ap,2}}{k_{ap,3}} = \left(\frac{[HCl]_{o,2}}{[HCl]_{o,3}}\right)^b$$

, take logarithms: $\ln\left(\frac{k_{ap,2}}{k_{ap,3}}\right) = b\ln\left(\frac{[HCl]_{o,2}}{[HCl]_{o,3}}\right)$ and isolate:

$$\boxed{b = \frac{\ln k_{ap,2} - \ln k_{ap,3}}{\ln[HCl]_{o,2} - \ln[HCl]_{o,3}}} \qquad (10)$$

5. Calculate the absolute rate constant with its random error. With the values of a and b (a=b=1), apply equation (3) for each series and obtain the following expression:

$$\boxed{k_i = \frac{k_{ap,i}}{[Acet]_{o,i}\,[H^+]_{o,i}}} \qquad (11)$$

   Calculate the mean value $\overline{k}$ with the three k_i and the random error.

6. Deduce and discuss, from the concentration-time graphs and the apparent rate constants obtained for each series, the effect of acetone and HCl on the reaction rate.

7. Confirm that the proposed mechanism is in agreement with the experimental rate law obtained experimentally.