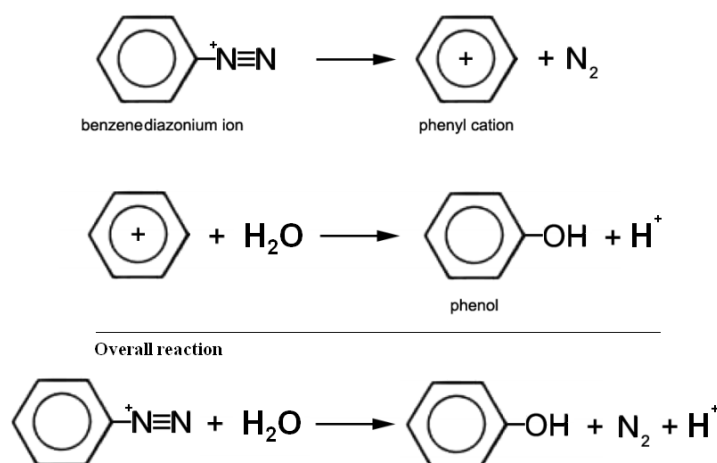


Chemical Kinetics of decomposition of benzene diazonium chloride

Introduction

Benzenediazonium chloride (BDC) is an organic compound with the formula $[C_6H_5N_2]Cl$. It is a salt of a diazonium cation and chloride. It exists as a colorless solid that is soluble in polar solvents.

BDC decomposes in aqueous solution to form phenol and N_2 gas as the following:



The rate law for the decomposition of BDC is given as:

$$R = k[BDC]^x[H_2O]^y$$

Since water exists in very large quantities (solvent) then the change in the concentration of water is assumed insignificant and then the rate law is written as:

$$R = k' [BDC]^x \quad \text{where} \quad k' = k[H_2O]^y$$

Experiments showed that the reaction order with respect to BDC is first order ($x = 1$ since it is a decomposition reaction).

The kinetics of the decomposition of BDC can be studied by monitoring the change of concentration of the BDC using spectroscopic methods or by monitoring the volume/pressure of N_2 gas evolved as a result of the reaction.

In this experiment the rate constant (k) will be determined at two different temperatures by measuring the volume of the evolved N_2 gas at constant pressure by time, and then calculate the activation energy and frequency constant for this reaction using Arrhenius equation.

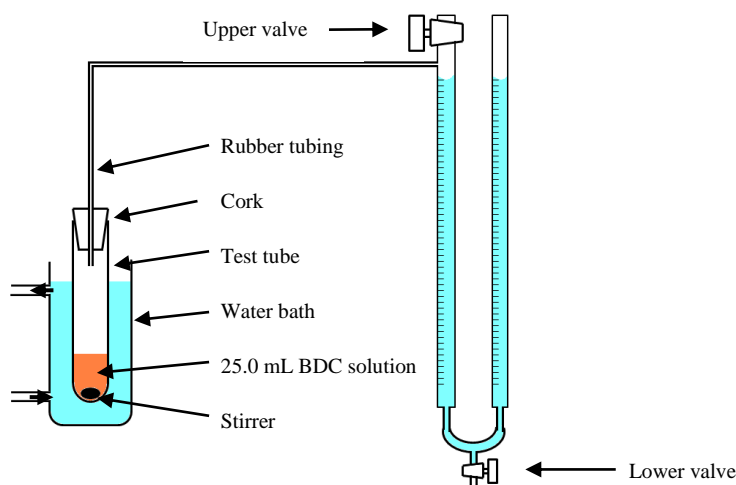
Experimental procedure

Preparation of the BDC solution:

Place a 500 mL flask in an ice bath, inside the flask add 3.25 mL of aniline and 11.0 mL of concentrated HCl. Slowly add 2.5 g of $NaNO_2$ dissolved in 40 mL water in to the flask, and then make up the volume to 500 mL by adding about 450 mL water. Mix and keep in the ice.

Preparing the system

1. Close the lower valve and open the upper valve of the experimental apparatus shown in the figure.
2. Fill the burets by adding water to the open burette up to zero in both sides (if the two burettes are not leveled fill up to zero of the burette connected to the rubber tube)
3. Place 25.0 mL of the BDC solution in the provided test tube, put the magnetic stirrer in the test tube, cork it tightly and then place the test tube in the water bath for about 10 minutes to reach thermal equilibrium as shown in the figure. Make sure that the stirrer is spinning.
4. After the 10 minutes have elapsed, close the upper stopper and start the stopwatch.



Data collection

5. The evolved nitrogen gas will push down the water in the left burette and therefore the water level in the other burette will rise. In order to have gas volume measurement at constant pressure, the water in both burettes must always be kept leveled by opening the lower valve and drawing the excess water.
6. Take volume measurement every two minutes for 40 minutes. Record these measurements in table 1 in the data sheet as volume (V_t) vs time (t).
7. After 40 minutes, lift the test tube from the water bath and place it in boiling water (or any temperature above 80°C). Leave the test tube there for 5 minutes, and then place the tube back in the water bath for another 10 minutes and take the volume measurement and record it as V_∞ in the data sheet.
8. Repeat the steps from 1 to 7 and set the thermostat at new temperature (10°C higher than trial 1).

Treatment of results

The integrated rate law of the decomposition of BDC is given as:

$$\ln \frac{[\text{BDC}]_t}{[\text{BDC}]_0} = -kt$$

The rate law is presented as a function of concentration of BDC (reactant), while the data collected are in terms of volume of N_2 evolved (product). Therefore volume measurements must be converted to express the concentration of BDC. Remembering that the volume and concentration are inversely proportional such as:

Volume at $t = 0$ is zero concentration at $t = 0$ is $[\text{BDC}]_0$ or at maximum concentration

Volume at $t = \infty$ is maximum volume concentration at $t = \infty$ is zero

As a result $[\text{BDC}]_0$ can be expressed in terms of V_∞ ($[\text{BDC}]_0 \propto V_\infty$). In the same manner the $[\text{BDC}]_t$ can be expressed in terms of $V_\infty - V_t$ ($[\text{BDC}]_t \propto V_\infty - V_t$). And hence, the integrated rate law is written as

$$\ln \frac{V_{\infty} - V_t}{V_{\infty}} = -kt$$

A plot of $\ln \frac{V_{\infty} - V_t}{V_{\infty}}$ vs t will result a linear line with slope = $-k$

Two experiments at two different temperatures will give two rate constants by which the activation energy and Arrhenius constant can be evaluated by the relation:

$$\ln \frac{k_1}{k_2} = \frac{-E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Once E_a is calculated one can use Arrhenius equation to calculate Arrhenius constant as

$$k_1 = Ae^{-E_a/RT_1}$$

Your report must include

- Signed data sheet
- Table shows $\ln \frac{V_{\infty} - V_t}{V_{\infty}}$ and t values for both trials
- Two graphs representing $\ln \frac{V_{\infty} - V_t}{V_{\infty}}$ vs t relation
- Calculated rate constants
- Calculated activation energy
- Calculated Arrhenius constant
- Error analysis

