Experiment

Object: Determine the *degree of hydrolysis* of urea hydrochloride by studying the hydrolysis of acid (HCl) catalyzed methyl acetate with equi-normal solution of urea hydrochloride.

Theory: The degree of hydrolysis of a salt is the fraction of the total salt hydrolyzed i.e. the ratio of the concentration of the free acid formed due to hydrolysis to that of which would have been produced if the hydrolysis is completed.
The concentration of the free acid formed during hydrolysis will be directly proportional to the rate constant k_1, of the reaction catalyzed by urea hydrochloride solution. Whereas the concentration of the acid that would be present after complete hydrolysis, will be directly proportional to rate constant, k_2, of the hydrolysis catalyzed by equimolar solution of HCl.

Therefore, degree of hydrolysis (α), is given by:

$$\boldsymbol{\alpha = \frac{k1}{k2}}$$

Schematically. The reaction can be represented as below:

$$\text{Urea} + \text{HCl} \longrightarrow \text{Urea hydrochloride salt}$$

$$(H_2N\text{-}CO\text{-}NH_2 + HCl) \longrightarrow (H_2N\text{-}CO\text{-}NH_3^+Cl^-)$$

Initial conc. C mol + C mol C mol

At any time during hydrolysis

$$\underset{c(1-\alpha)}{H_2N\text{-}CO\text{-}NH_3^+Cl^-} \longrightarrow \underset{c\alpha}{H_2N\text{-}CO\text{-}NH_2} + \underset{c\alpha}{HCl}$$

Therefore, hydrolysis reaction in presence of urea hydrochloride and only HCl are given as

$$H_3C\text{-}COOCH_3 + \underset{c\alpha}{HCl} \xrightarrow[NH_2CONH_2]{k_1} H_3C\text{-}COOH + CH_3OH$$

$$H_3C\text{-}COOCH_3 + \underset{c}{HCl} \xrightarrow{k_2} H_3C\text{-}COOH + CH_3OH$$

$$\boldsymbol{k1 \propto c\alpha, \quad k2 \propto c}$$

$$\boldsymbol{\frac{k1}{k2} = \alpha}$$

Requirements:

1. 0.5 N HCl
2. 0.5 N ureahydrochloride (50mL 0.5N HCl +1.5g Urea)
3. 0.1 N NaOH
4. Phenolphthalein indicator
5. Ice Cold water
6. Burette (25 ml capacity), Pipette (2 ml)
7. Titration flask - 0ne 100 ml.
8. Beaker containing ice cold water.

Procedure:

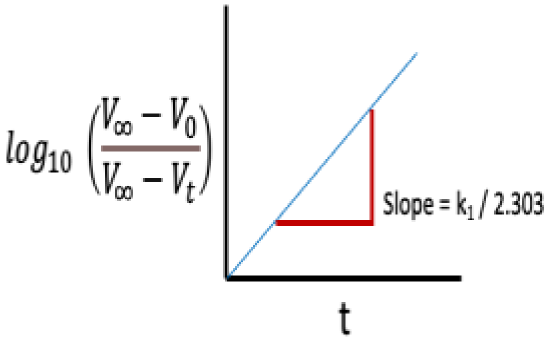
A. Prepare a reaction mixture by mixing 2ml methyl acetate and 50 ml 0.5 N urea hydrochloride solution and determine the rate constant k_1, of the reaction at laboratory temperature as follows:

1. While mixing methyl acetate (2ml) and urea hydrochloride solution (0.5 N) 50 ml, (Note 1) start the stopwatch and immediately take 2 ml of this mixture. Transfer it in a titration flask containing about 20 ml ice cold water and ~2 drop of phenolphthalein indicator.
2. Titrate it with 0.1N NaOH solution taken in the burette.
3. Note the volume of NaOH required, this gives V_0 value. i.e. volume of NaOH required at t = 0 (means hydrolysis has not yet started).
4. Similarly titrate 2 ml of the reaction mixture after every about 10 minute interval of time (note down the 'exact time interval') upto 60 minute and note the volumes of NaOH required (denoted by: V_t).
5. In the end, heat the remaining reaction mixture in a water bath maintained at about 80 ^oC for about 40mints and cool it down.
6. Take 2 ml of this mixture and titrate it with the same NaOH solution to get volume of NaOH required at the end of the reaction. Record this volume of NaOH as V_∞.
7. As the reaction follows first order kinetics, we will you be using the following formula to calculate the rate constant, here, k_1.
8. Preparation of 0.5 N Urea hydrochloride solution: Weigh 1.5 g urea and dissolve it in a 0.5 N HCl solution and make the volume upto 50 ml. The resulting solution will be 0.5 N Urea hydrochloride solution keep this solution as such for half hour, before use.

$$k_1 = \frac{2.203}{t} log_{10} \left(\frac{a}{a-x}\right)$$

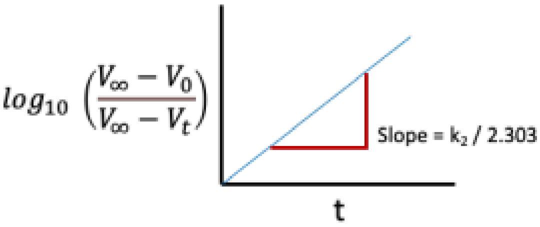
replaced by

$$k_1 = \frac{2.203}{t} log_{10} \left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$



B. Repeat the same experiment with 2 ml of ester solution and 50 ml 0.5N HCl solution (instead of urea hydrochloride solution) at the laboratory and determine the rate constant (k_2) in the same way using the following equation.

$$k_2 = \frac{2.203}{t} log_{10} \left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$



The ratio of $\frac{k_1}{k_2}$ gives the degree of hydrolysis of the salt (i.e. urea hydrochloride).

Evaluate $k_1 and\ k_2$ by graphically and get the ratio of $\frac{k_1}{k_2}$ i.e. α.

Observation Table

1. Table for titration of solution containing 50mL 0.5 N HCl having 1.5 g Urea + 2 ml methyl acetate.

$V_0 =\quad mL,\quad V_\infty = \ ...mL$

$V_\infty - V_0$ = ... mL

Sl.No.	Time (min.)	Volume of NaOH solution (ml)	$V_\infty - V_t$	$log_{10} \left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$	$k_1 = \frac{2.203}{t} log_{10} \left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$
1.	10	V_{10}	$V_\infty - V_{10}$		
2.	20	V_{20}	$V_\infty - V_{20}$		
3.	30	V_{30}	$V_\infty - V_{30}$		
4.	40	V_{40}	$V_\infty - V_{40}$		
5.	50	V_{50}	$V_\infty - V_{50}$		

2. Table for titration of solution containing 50ml 0.5 N HCl + 2ml methyl acetate:

$V_0 = \quad mL, \quad V_\infty = \ ...mL$

$V_\infty - V_0 =$ … mL

Sl.No.	Time (min.)	Volume of NaOH solution (ml)	$V_\infty - V_t$	$log_{10}\,(\frac{V_\infty - V_0}{V_\infty - V_t})$	$k_2 = \frac{2.203}{t}\,log_{10}\,(\frac{V_\infty - V_0}{V_\infty - V_t})$
1.	10	V_{10}	$V_\infty - V_{10}$		
2.	20	V_{20}	$V_\infty - V_{20}$		
3.	30	V_{30}	$V_\infty - V_{30}$		
4.	40	V_{40}	$V_\infty - V_{40}$		
5.	50	V_{50}	$V_\infty - V_{50}$		

Conclusion: The degree of hydrolysis (α) of urea hydrochloride salt hydrolysis is found to be XX.

Note 1:

$H_2N\text{-}CO\text{-}NH_2$
M = Mol. Wt. = 60
E = Eq. Wt. = 60

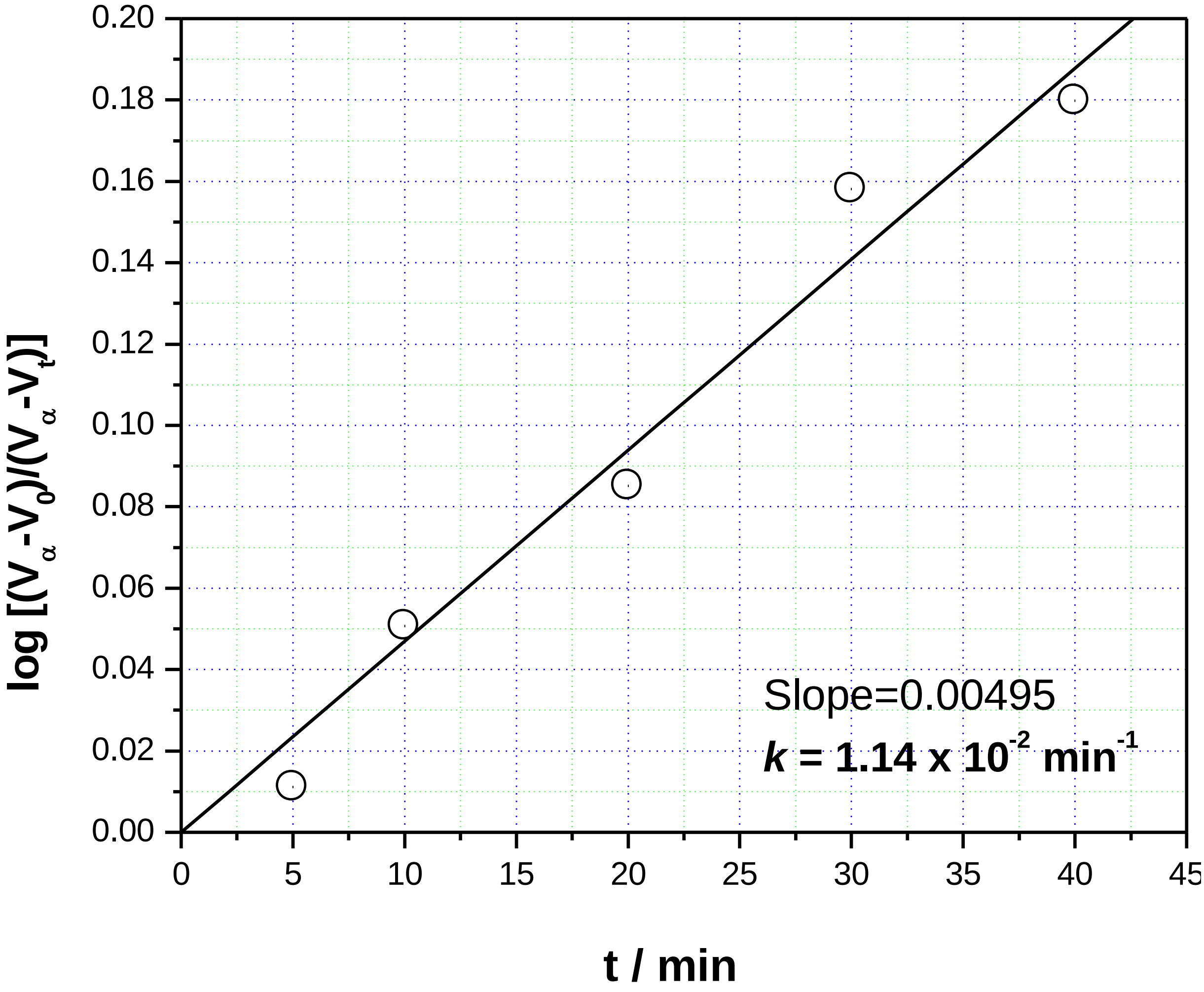
Amount of urea required to prepare 0.5 N Urea solution

$$\boldsymbol{m = (\frac{EVN}{100})}$$

$$\boldsymbol{m = (\frac{60\ X\ 50\ X\ 0.5}{100})}$$

$$\boldsymbol{m = 1.5\ g}$$

Note 2:



0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
log [(Vα-V0)/(Vα-Vt)]
0 5 10 15 20 25 30 35 40 45
t / min
Slope=0.00495
k = 1.14 x 10-2 min-1