Question

Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below:

t (min)	0	30	60	90
C (M)	0.85	0.8004	0.7538	0.7096

Show that it follows a pseudo first order reaction as the concentration of water remains nearly constant (55 mol L^{-1}) during the course of the reaction. What is the value of k' in this equation

Rate = $k'[CH_3COOCH_3][H_2O]$

Answer:

$CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH$

methyl acetate — acetic acid — methanol

This is a second order reaction with rate law expression:

Rate = $k'[CH_3COOCH_3][H_2O]$

As concentration of water remains nearly constant

Rate = $k[CH_3COOCH_3]$, $k = k'[H_2O]$

This is a pseudo first order reaction.

$$k = \frac{2.303}{t} \log \frac{[ester]_{t=0}}{[ester]_{t=t}}$$

At t = 30 min

$$k = \frac{2.303}{30} \log \frac{0.85}{0.8004} = 2 \times 10^{-3} \text{ min}^{-1}$$

At $t = 60$ min

$$k = \frac{2.303}{60} \log \frac{0.85}{0.7538} = 2 \times 10^{-3} \text{ min}^{-1}$$

At $t = 90$ min

$$k = \frac{2.303}{90} \log \frac{0.85}{0.7096} = 2 \times 10^{-3} \text{ min}^{-1}$$

As experimental observations give same value of k for three different time intervals, this verifies that the reaction behaves as first order reaction

$$k'[H_2O] = k = 2 \times 10^{-3}$$

$$k' \times 55.5 = 2 \times 10^{-3}$$

$$k' = 3.6 \times 10^{-5} \text{ mol}^{-1} \text{ L min}^{-1}$$

Question

In a pseudo first order hydrolysis of ester in water, the following results were obtained:

t/s	0	30	60	90
Cster (M)	0.55	031	0.17	0.085

i) Calculate the average rate of reaction between the time interval 30 to 60 s.

ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

Answer: $\underset{\text{ester}}{RCOOR'} + H_2O \rightarrow \underset{\text{acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH}$

i) Average rate of reaction $= -\frac{([\text{ester}]_{t=t_2} - [\text{ester}]_{t=t_1})}{t_2 - t_1}$

for $t_2 = 60$s, and $t_1 = 30$s

Average rate of reaction $= -(0.17 - 0.31)$

Average rate of reaction $= -\frac{(0.17 - 0.31)}{60 - 30}$

$= 4.67 \times 10^{-3}$ mol $L^{-1} s^{-1}$

ii) This is a psedo first order reaction, with rate law expression as:

$R = k'[H_2O][CH_3COOCH_3]$ (k)

$Rate = k[CH_3COOCH_3]$

where k is psedo first order rate constant

$$k = \frac{2.303}{t} \log \frac{[ester]_{t=0}}{[ester]_{t=t}}$$

At $t = 30s$

$$k = \frac{2.303}{30} \log \frac{0.55}{0.31} = 1.911 \times 10^{-2} s^{-1}$$

At $t = 60s$

$$k = \frac{2.303}{60} \log \frac{0.55}{0.17} = 1.957 \times 10^{-2} s^{-1}$$

At $t = 90s$

$$k = \frac{2.303}{90} \log \frac{0.55}{0.085} = 2.075 \times 10^{-2} s^{-1}$$

Taking average of above three experimental values of k

$$k = \frac{1.911 \times 10^{-2} + 1.957 \times 10^{-2} + 2.075 \times 10^{-2}}{3} = 1.98 \times 10^{-2} s^{-1}$$

Question

Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law with $t_{1/2} = 3$ hrs. What fraction of sample of sucrose remains after 8 hours?

Answer:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

sucrose — glucose — fructose

this is a pseudo first order reaction with rate law expression $Rate = K[C_{12}H_{22}O_{11}]$

$$K = \frac{2.303}{t} \log \frac{[C_{12}H_{22}O_{11}]_{t=0}}{[C_{12}H_{22}O_{11}]_{t=t}}$$

for first order reaction $t_{1/2} = \frac{0.693}{K}$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{[C_{12}H_{22}O_{11}]_{t=0}}{[C_{12}H_{22}O_{11}]_{t=t}}$$

$$\frac{0.693}{3} = \frac{2.303}{8} \log \frac{[C_{12}H_{22}O_{11}]_{t=0}}{[C_{12}H_{22}O_{11}]_{t=t}}$$

$$\log \frac{[C_{12}H_{22}O_{11}]_{t=0}}{[C_{12}H_{22}O_{11}]_{t=t}} = 0.8024$$

$$\log \frac{[C_{12}H_{22}O_{11}]_{t=t}}{[C_{12}H_{22}O_{11}]_{t=0}} = -0.8024$$

$$\frac{[C_{12}H_{22}O_{11}]_{t=t}}{[C_{12}H_{22}O_{11}]_{t=0}} = \text{antilog}(-0.8024) = 0.158.$$

Thus the fraction of sample of sucrose that remains after 8 hrs is 0.158