Determination of the rate constant and the activation Energy of ester hydrolysis reaction

The rate, *v*, of the second order reaction

$$A + B \rightarrow C \qquad [1]$$

Is proportional to the concentration of each reactant raised to the first power:

$$v = k_T[A][B] \qquad [2]$$

The coefficient *k* is the **rate constant** of the reaction and the expression [2] is called the rate law of reaction. To define the rate constant we can use the concentration of the reactants or the product(s):

$$v = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} \qquad [3]$$

For equal concentrations of the reactants, [A]=[B], and using eq. 3, the rate law of the reaction [1] can be written

$$v = -\frac{d[A]}{dt} = -k[A]^2 \qquad [4]$$

Its integrated form is

$$kt = \frac{1}{[A]} - \frac{1}{[A]_0} \qquad [5]$$

where $[A]_0$ denotes the concentration of the reactants at t=0.

The example of the second-order reaction is the very early stage of ester (ethyl acetate) hydrolysis.

$$CH_3COOC_2H_5 + OH^- \rightleftarrows CH_3COO^- + C_2H_5OH \qquad [6]$$

When the initial concentrations of reactants are equal, $[\text{ester}]_0 = [OH^-]_0 = [A]_0$, the integrated rate law is given by equation [5]. After simple transformation this equation takes the form

$$k_T = \frac{1}{t[A]_0} - \frac{[A]_0 - [A]}{[A]_0} \qquad [7]$$

where the subscript T indicates the temperature of the reaction.

According to the reaction [6] the ions OH^- and CH_3COO^- give rise to the overall electrical conductance. As the conductance of OH^- , G_{OH-}, is several times higher than that of CH_3COO^-, $G_{CH3COO-}$, we can monitor the progress of the reaction by measuring the conductance of the solution. The overall conductance at time t is a sum of the both kinds of ions multiplied by the corresponding mole fraction and the constant conductance of cations, G_{M+}, which are also present in the reaction solution:

$$G_t = G_{OH-}\frac{[A]}{[A]_0} + G_{CH3COO-}\frac{[A]_0 - [A]}{[A]_0} + G_{M+} = (G_{OH-} + G_{M+})\frac{[A]}{[A]_0} + (G_{CH3COO-} + G_{M+})\frac{[A]_0 - [A]}{[A]_0} \qquad [8]$$

It is convenient to write [8] in the form

$$G_t = G_0\frac{[A]}{[A]_0} + G_\infty\frac{[A]_0 - [A]}{[A]_0} \qquad [9]$$

where G_0 indicates the conductance of the solution at t=0 while G_∞ the conductance when the reaction would theoretically procced to the end. Simple theoretical transformation of eq. [9] leads to the expression for $[A]_0/[A]$;

$$\frac{[A]}{[A]_0} = \frac{G_0 - G_\infty}{G_t - G_\infty} \qquad [10]$$

which can be used to the expression the rate constant [7] in terms of conductance.

As

$$\frac{[A]_0-[A]}{[A]_0}=\frac{[A]_0}{[A]}-1=\frac{G_0-G_t}{G_t-G_\infty} \qquad [11]$$

Eq. [7] can take the form

$$k_T=\frac{1}{t[A]_0}\frac{G_0-G_t}{G_t-G_\infty} \qquad [12]$$

The conductance G_0 and G_t are easy to measure during the experiment. The problem is with G_∞ at the reaction [6] does not proceed to the end but stops when reach equilibrium. We can overcome this problem noting that eq. [12] can be transformed into the form

$$G_t=G_\infty+\frac{1}{k_T[A]_0}\frac{G_0-G_t}{t} \qquad [13]$$

Now, we can fit a straight line, $y=a+bx$, to the G_t vs $(G_0-G_t)/t$ data and calculate the rate constant from the slope, b.

The temperature dependence of the rate constant is given by the Arrhenius equation

$$k_T=Ae^{-E_a/RT} \qquad [14]$$

where E_a is an activation energy for given temperature. When the rate constants are known for two different temperatures T_1 and T_2, one can create a set of equations

$$lnk_{T1}=\ln A-\frac{E_a}{RT_1}$$

$$lnk_{T2}=\ln A-\frac{E_a}{RT_2} \qquad [15]$$

and solve it for activation energy. Activation energy is the minimum kinetic energy that the reactants must have in order to form products. The higher the activation energy, the stronger the influence of temperature on the rate constant and the rate of reaction.

Experiment

1. Switch the thermostat on and set up the temperature at approximately 30^{o}C.

2. Pipette $40cm^3$ of 0.02M CH3COOC2H5 solution into one baker and the same amount of 0.02M NaOH into another one. Place both bakers into the thermostat bath.
3. Switch on the conductometer. Wash up the conductivity electrode in the distilled water, shake the electrode won to remove the excess of water, and place the electrode in one solution (to warm it up).
4. Read the temperature after 15 minutes of heating the solutions.
5. Mix both solutions together and stir the resulting solution properly.
6. Read G0 immediately after mixing solutions. Do not forget to dip the electrode for several times in the examined solutions before each conductance measurements. Read out the conductance, Gt, at intervals of 3 minutes in the time 30 minutes. Note down the readings in a table.
7. Repeat the measurements at 50°C using newly made CH3COOC2H5 and NaOH solutions and calculate activation energy.

Table 1

Collections the results

t [s]	G_t [S]	$(G_0 - G_t)/t$ $[S \cdot s^{-1}]$
180		
360		
540		
….		
1800		