Reaction Second Order

Kinetic Experiments:

- **Alkaline Hydrolysis of Esters**

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Relationship between concentration and conductivity

The specific conductance κ of the reaction mixture is determined by the presence of the free mobile ions. κ involves the respective molar conductivities of the ions (λ_i) and the corresponding molar ion concentrations ($\mathbf{c_i}$):

$$\kappa = \lambda_{OH}\, \mathbf{c_{OH}} + \lambda_A\, \mathbf{c_A} + \lambda_{Na}\, \mathbf{c_{Na}} \tag{1}$$

The concentration of the hydroxide ions ($\mathbf{c_{OH}}$) **x** is indicated by **x**, the initial concentration by $\mathbf{x_0}$. Thus, due to the reaction equation the concentration of the carbonic acid anions ($\mathbf{c_A}$) is given by

$$\mathbf{c_A = x_0 - x} \tag{2}$$

Equation **(1)** becomes to:

$$\kappa = (\lambda_{OH} - \lambda_A)\, \mathbf{x} + \lambda_{Na}\, \mathbf{c_{Na}} + \lambda_A\, \mathbf{x_0} \tag{3}$$

Using the constants

$$A = (\lambda_{OH} - \lambda_A) \qquad \text{and} \qquad B = \lambda_{Na}\, \mathbf{c_{Na}} + \lambda_A\, \mathbf{x_0}$$

is obtained:

$$\kappa = A\mathbf{x} + B \qquad \text{or} \qquad \mathbf{x} = \frac{\kappa - B}{A} \tag{4}$$

Considering the conductance at the beginning of the reaction κ_0 yields:

$$\kappa_0 = A\mathbf{x_0} + B \qquad \text{or} \qquad \mathbf{x_0} = \frac{\kappa_0 - B}{A} \tag{5}$$

$$\frac{\mathbf{x_0}}{\mathbf{x}} = \frac{\kappa_0 - B}{\kappa - B} \tag{6}$$

If the initial concentration of the ester than the initial concentration of the hydroxide solution, then the hydroxide ions will be used up at the end of the reaction.

When $\mathbf{t} = \infty$ then $\mathbf{x = 0}$

and in accordance to equation **(4)**

$$B = \kappa_\infty \qquad (7)$$

Substituting equation **(7)** into equation **(6)** gives:

$$\frac{x_0}{x} = \frac{\kappa_0 - \kappa_\infty}{\kappa - \kappa_\infty} \qquad (8)$$

Thus the correlation between the concentration $\mathbf{c_{OH}} = \mathbf{x}$ and the conductivity is made.

Concentration change with time

Starting point for the study of the **alkaline ester hydrolysis** is the theoretical approach of a **second order reaction**.

Second-order rate laws involve two reactants, and for both of them concentration will depend upon time.

The change in the concentration of hydroxide ions ($\mathbf{c_{OH}}$) with time is defined as follows

$$\frac{dc_{OH}}{dt} = -k \cdot c_{OH} \cdot c_E \qquad (9)$$

k = rate constant
$\mathbf{c_E}$ = concentration of the ester.

Because equivalent amounts of ester and hydroxide are reacting, $\mathbf{c_E}$ can be expressed in terms of the hydroxide ion concentration ($\mathbf{c_{OH} = x}$).

$$c_E = a - (x_0 - x) \qquad (10)$$

$\mathbf{x_0}$ = initial concentration of the hydroxide solution
a = initial concentration of the ester

Combining equation **(10)** and equation **(9)** gives:

$$\frac{dx}{dt} = -k \cdot x \cdot (a - x_0 + x) \qquad (11)$$

The separation of the variables yields the following expression:

$$\int_{x_0}^{x} \frac{dx}{x \cdot (a - x_0 + x)} = -k \int_{t_0}^{t} dt \qquad (12)$$

The symbol **x** is used both for the integration variable and for its upper limit.

Provided that $a \neq x_0$, partial fraction decomposition: of the integrand on the left hand-side of equation **(12)** and integration yields:

$$\ln \frac{x_0 \cdot (a - x_0 + x)}{a \cdot x} = (a - x_0) \cdot k\,t \qquad (13)$$

The reaction conditions of the alkaline ester hydrolysis ($a = 2x_0$) allow to simplify equation **(13)**:

$$\ln\left[\frac{1}{2}\left(\frac{x_0}{x} + 1\right)\right] = x_0 \cdot k\,t \qquad (14)$$

By considering equation **(8)** the above expression my be rewritten as:

$$\ln\left[\frac{1}{2}\left(\frac{\kappa_0 - \kappa_\infty}{\kappa - \kappa_\infty} + 1\right)\right] = x_0 \cdot k\,t \qquad (15)$$

This represents the equation of a straight line, whose slope is identical with $x_0 \cdot k$.

If the decrease in the concentration of the hydroxide ions is monitored by **pH probe measurement**, the following relation is used:

$$\frac{x_0}{x} = \frac{c_{OH(0)}}{c_{OH}} \qquad (16)$$

$$c_{OH(0)} = \frac{K_W}{c_{H(0)}} \quad \text{and} \quad c_{OH} = \frac{K_W}{c_H} \qquad (17)$$

K_W = equilibrium constant for the autoionization of water.

Substituting **(17)** into equation **(16)** yields:

$$\frac{x_0}{x} = \frac{c_H}{c_{H(0)}} = \frac{10^{-pH}}{10^{-pH(0)}} = 10^{pH(0) - pH} \qquad (18)$$