

A 32 Saponification Rate Constant of an Ester

Task:

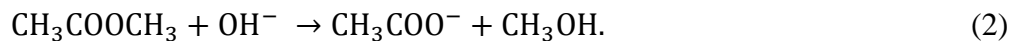
Determine the Reaction Rate Constant k for the saponification of Methyl Acetate at two given temperatures, and from this calculate the prefactor as well as the activation energy based on the Arrhenius equation.

Basics:

The saponification of an ester occurs generally in accordance with the reaction equation:



In the case of the methyl acetate:



The reaction is 2nd order, it's kinetic can be described with the following ansatz:

$$\frac{dx}{dt} = k(a - x) \cdot (b - x). \quad (3)$$

Whereby a and b are the concentrations of the precursors AB or C at time $t=0$, and x is the concentration of one of the reaction products. Integration results in equation (4):

$$k \cdot t = \frac{1}{a-b} \ln \frac{(a-x)b}{(b-x)a} = \frac{2.303}{a-b} \cdot \lg \frac{(a-x)b}{(b-x)a}. \quad (4)$$

The temperature dependency of the rate constants will, in most cases, be described by the empirically determined Arrhenius equation:

$$k = A \cdot \exp\left(\frac{-E_A}{R \cdot T}\right). \quad (5)$$

Here, A is the prefactor or pre-exponential factor, E_A the activation energy, T the temperature, and R the universal gas constant. The activation energy is defined by Arrhenius as:

$$\frac{d \ln k}{d \frac{1}{T}} = - \frac{E_A}{R}. \quad (6)$$

In our example of the saponification of methyl acetate (equation (2)) we initially insert the concentration of the formed acetate-ion for x , the initial concentration of the ester for a , and the OH^- -ion concentration for b into the equation.

As the relatively fast moving OH^- -ion will be replaced by the less mobile acetate-ion during the reaction, the kinetic can be easily traced by the measurement of the electrical conductivity. According to the Kohlrausch Law for the measurement of the specific conductivity κ at a random time equation (7) applies:

$$\kappa = \{\lambda_{Na}b + \lambda_{OH}(b - x) + \lambda_{Ac}x\} \cdot 10^{-3} \left[\frac{1}{\Omega \cdot cm} \right] \quad (7)$$

where λ_{Na} , λ_{OH} , and λ_{Ac} are the equivalent conductivities of the corresponding ions. The concentration of the Na^+ -ion is constant throughout the experiment, and is equal to the initial concentration of the OH^- -ion. The concentration of the formed acetate ion is given by:

$$x(t) = \frac{(\kappa_b - \kappa(t))}{\lambda_{OH} - \lambda_{Ac}} = \frac{\kappa_b - \kappa(t)}{\Delta\lambda}. \quad (8)$$

The initial conductivity is given by:

$$\kappa_b = \kappa(t = 0) = (\lambda_{Na} + \lambda_{OH})b. \quad (9)$$

With this correlation the initial concentration b can be determined by the conductivity measurement. Whereby the, in the experiment occurring, concentration must be set:

$$\lambda_{Na} + \lambda_{OH} = \left\{ 198 + \frac{3.7}{^\circ C} (\vartheta - 18^\circ C) \right\} \left[\frac{cm^2}{\Omega \cdot mol} \right]. \quad (10)$$

ϑ = Experimental temperature in $^\circ C$

The initial concentration a of the ester is, after complete conversion, equal to the total amount of the formed acetate-ion. Thus we get a by inserting the value a for x and the corresponding end-conductivity κ_a in equation (7), which gives:

$$x(t = \infty) = a = \frac{\kappa_b - \kappa_a}{\Delta\lambda}. \quad (11)$$

Strictly speaking, the λ -values, and therefore also $\Delta\lambda$, vary somewhat with the concentration during the reaction. A good approximation gives:

$$\Delta\lambda = \left\{ 135 + \frac{2.1}{^\circ C} (\vartheta - 18^\circ C) \right\} \left[\frac{cm^2}{\Omega \cdot mol} \right]. \quad (12)$$

In this way, the variables a , b , and x of rate equation (3) can be calculated from conductivity.

Experimental Procedure:

After cleaning with distilled water, insert 50 ml 0.1 m NaOH solution into a resistance vessel, dilute it up to exactly a half and determine the specific κ_b at 20°C. Subsequently, add 0.2 ml methyl acetate solution and begin measuring the time. The temporal changes of the conductivity $\kappa(t)$ will be recorded at a constant temperature, where a measurement will be taken at the beginning of each minute. After approximately half an hour the conductivity will stay constant, this is the end conductivity κ_a . Repeat the experiment at 30°C. After use, wash the measuring electrode and place it in a glass beaker with distilled water.

Data Analysis:

From the measured specific conductivity κ_a and κ_b respectively you can calculate the concentrations b and a according to equations (9) and (11). Using equation (8), the measured $\kappa(t)$ values give the concentration of the formed acetate-ion at each time step. These values will be tabulated together with the measured times and, using equation (4), the equivalent rate constant k calculated. An error discussion should be carried out for the thus calculated rate constants. After checking that the values show only statistical scattering, average over the values for each of the two temperatures and determine the error for k. From the determined k-values at both temperatures, calculate, using equation (5), the activation energy E_A and the prefactor A of the reaction. Complete an error calculation for both parameters. Take all potentially flawed variables into account.

What you should know:

- Reaction Order and molecularity of a reaction
- Differential rate laws and their integration
- Parallel and consecutive reactions
- Chain reactions with and without branching
- Basics of the methods of calculating rate constants (Collision theory, Activated complex theory)

Extra Question:

Discuss the mechanism of ester saponification and justify why it is a 2nd Order reaction!